Results of the Analyses of Surface Soil Samples from Near Decatur, Alabama for Fluorinated Organic Compounds

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Abstract: In March 2009, soil samples were collected from six agricultural fields near Decatur, Alabama area where sludge from the Decatur Utilities had been applied for more than 12 years. Two soil samples were also collected at one background field, an area where sludge had not been applied. These samples were analyzed for a variety of perfluorinated chemicals (PFCs) and fluorotelomer alcohols (FTOHs). Samples from five of the sludge-applied fields had soil concentrations of PFCs and selected FTOHs exceeding the background sample levels. The soil samples from one field where sludge had been applied at relatively limited rates had levels similar to the background field samples.

Key findings include:

- Perfluorooctanoic acid (PFOA) levels ranged from 50-320 ng/g soil (or parts per billion, ppb), two to three orders of magnitude above background
- Perfluorooctane sulfonate (PFOS) levels ranged from 30-410 ng/g soil (ppb), one to two orders of magnitude above background
- Perfluorodecanoic acid (PFDA or C10) levels ranged from 130-990 ng/g (ppb) and perfluorododecanoic acid (PFDoA or C12) levels ranged from 30-530 ng/g (ppb). Levels for these two PFCs were the highest observed, both at least two orders of magnitude above background
- 8:2 FTOH levels ranged from 4-80 ng/g (ppb), one to two orders of magnitude above background. (8:2 FTOH can degrade to PFOA)
- 10:2 FTOH levels ranged from 4-150 ng/g (ppb) and 12:2 FTOH levels ranged from 2-160 ng/g (ppb), one to three orders of magnitude above background. 10:2 FTOH and 12:2 FTOH (which can degrade to PFDA and PFDoA, respectively) were the highest FTOHs generally observed.

1. Introduction

For the last 12 years, Decatur Utilities, of Decatur, AL, has been authorized to apply sewage sludge on about 5000 acres of local agricultural land (Neill, 2009a). The United States Environmental Protection Agency (USEPA) collected (Neill, 2007) and analyzed (Washington, 2009) a limited number of sludge and soil samples from this operation. The results documented the presence of several fluorotelomer alcohol (FTOH) and perfluorinated compounds (PFCs) in the land application soil samples.

The USEPA subsequently collected (November 13, 2008) and analyzed drinking water samples from a few Decatur, AL public drinking water supplies (Neill, 2009a). No levels of the perfluorooctanoic acid (PFOA) or perfluorooctane sulfonate (PFOS) were observed above the Provisional Health Advisories (USEPA, 2009) in these municipal drinking water samples (Washington et al., 2008a). In February 2009, the USEPA collected additional water samples from selected private wells, field wells, agricultural ponds, and surface waters located in and immediately around the land application fields. Elevated levels of some PFCs (Lindstrom et al., 2009) were found in some of these samples.

Additional samples of surface soils were collected in March 2009 to characterize the extent and magnitude of the PFC contamination in the land application area (Neill, 2009a). This report summarizes the analytical methodologies employed and the results of analysis on the surface soil samples for targeted PFCs and FTOHs.

2. Methods

2.1 Sample Collection

Soil samples were collected by USEPA Region 4 personnel during the period March 23-25, 2009 following the procedures described in the USEPA Region 4 Quality Assurance Project Plan (Neill, 2009b) and the corresponding trip report (Neill, 2009c). Table 1 list the sample identification number and description for the soil samples collected at the six sampling sites where the sludge was applied, the background site, and the quality control (QC) samples.

The sampling equipment was supplied and prepared by scientists from Region 4's Science and Ecosystem Support Division (SESD) and the National Exposure Research Laboratory's Ecosystems Research Division (NERL/ERD), both located in Athens, GA. The sampling equipment was constructed of stainless steel materials and washed three times with Optima-grade methanol (MeOH) prior to and between uses. Soil samples at the 0-10 cm interval were collected using spoons, hand augers, and pans. The soil samples were stored individually in certified-clean, 500 mL, wide-mouth high-density polyethylene (HDPE) containers. The sample containers and the MeOH-washed sampling equipment were determined to be free of contamination for the intended analytes before the sampling trip.

2.2 Sample Storage, Preparation and Analysis

Region 4 staff transported and delivered the field samples to NERL/ERD personnel, documented by Chain of Custody forms (Neill, 2009c). The samples were securely stored in controlled-access laboratories within the secure main NERL/ERD building. The samples were extracted as described in the Standard Operating Procedures (SOPs) No. PMB-58.0 and PMB-59.0 (Appendices 1 and 2, respectively). Brief summaries of the methods follow:

Field-moist soil samples were homogenized by repeatedly passing them through 2-mm, stainless-steel sieves, coning and quartering until the sample was reduced to four approximately 1-g aliquots. Each of the four aliquots was transferred to a pre-cleaned and labeled 16-mL polycarbonate (PPCO) centrifuge tube and sealed with a press-on cap.

The extraction and analysis methods for sludge-applied soils were based on the SOPs that were part of the existing QAPP with modifications based on our previous study of Decatur soils (Washington et al., 2009). Specifically, the remaining in-stock sludge-applied Decatur soils from the 2007/2008 study were used to optimize the extraction techniques. The improved extraction techniques entail performing multiple extractions of each sample and combining the extracts in an effort to exhaust the samples of the target analytes. These changes were incorporated in the existing SOPs included as appendices to this report. Two aliquots of each sample were extracted for FTOH analysis via gas chromatograph/mass spectrometer (GC/MS). Two additional aliquots were extracted for PFC analysis via liquid chromatograph/tandem mass spectrometer (LC/MS/MS).

2.2.1 Liquid Chromatograph, Tandem Mass-Spectrometer Analyses: Acetonitrile/water extracts of the soil aliquots were analyzed on a Waters Quattro Premier XE tandem mass spectrometer interfaced with a Waters Acquity ultra-performance liquid chromatograph (UPLC). Typical mass chromatograms for the carboxylic acid and sulfonate analytes are depicted in Figure 1a and 1b, respectively. As Figure 1 depicts, some analytical peaks were complex. We integrated these peaks by setting software integration parameters so that integrations closely approximated the integration rules described in detail in Washington et al. (2007). All software-integrated peaks were checked and, if needed, adjusted manually according to these same integration rules. Additional information regarding the analysis parameters is presented in Appendix 3. Efforts were made to reduce background noise in the system for PFOA by modifying the UPLC plumbing. Modifications included installation of PEEK tubing, removal of the degasser, installation of a C18 trap column (100mm × 2.1mm × 3.5µm) in the water eluent line immediately upgradient of the solvent mixer, and use of manually-degassed 18 MΩ water ”polished” by passing through a Waters HLB solid phase extraction cartridge (Washington et al., 2008b).

While preparing for sample analysis, it was discovered that the UPLC could not maintain a sufficiently stable eluent pressure. It was determined that the only way to achieve satisfactory pressure stability, within an acceptable sample-analysis timeframe, was to remove the trap column. With the trap column removed, the operating pressure range dropped to acceptable levels and stabilized the pressure variability. However, this altered the elution time windows for the analytes. Consequently, revised analytical and quantitation methods had to be developed for

these samples (Tables 2 and 3). These revised methods maintained compliance with the quality criteria for precision of the calibrations as defined in the QAPP.

Twenty microliters of extract were introduced to a Waters BEH C18 guard cartridge followed by a Waters BEH C18 analytical column, 100mm × 2.1mm × 2.1µm, maintained at 35 ^{o}C. The UPLC was operated using ACN and water eluents adjusted to pH 4 with glacial acetic acid. After UPLC elution, extracts were introduced to the mass spectrometer operated in ESI(-) mode.

Quantitation was performed using mass-labeled matrix internal standards. Quantitation for C6, C8 ($^{13}C_4$-PFOA), C9, C10, C11, and C12, analytes was accomplished using isotopic dilution since isotopically labeled standards were available. C7 and PFOS were quantitated using the mass-labeled C8 ($^{13}C_4$-PFOA) and $^{13}C_2$-PFDA matrix internal standards, respectively. Calibrations were constructed with linear regressions of untransformed data, and plots of peak area/internal standard area versus calibration standard concentration/ internal standard area; 1/X weighting was applied for regression. Standards injected on the instrument ranged from 0.9 to 4800 pg/g. The lowest standard concentrations that were used to generate the calibration curves were those levels for which the calibration lines maintained a central tendency for repeated measures of the standards. Final calibration curves consisted of 11-14 standard concentrations of the targeted species spanning from 5 to 4800 pg/g. Standards were interspersed with sample extracts and blanks throughout the sample analysis runs. The limit of quantification (LOQ) was designated as the value of the lowest standard for which average standard readings included in the calibration are within the specified quality criterion of ± 30% (Table 3) of the prepared standard value. The sample extract dilution factors are summarized in Table 1**.** The efficacy of the acids extractions was monitored using $^{13}C_8$-PFOA as a recovery internal standard. Soil concentrations of the targeted PFCs were calculated from analytical extract values for the samples compared to the standards**.**

2.2.2 Gas Chromatograph, Mass Spectrometer Analyses: Methyl *tert*-butyl ether (MTBE) extracts of the soil aliquots were analyzed on an Agilent Technologies GC system equipped with a mass selective detector (MSD). The MSD was operated in the positive chemical-ionization mode with methane reagent gas. Compound separation and quantification were performed on a Restek Rtx-1701 capillary column (30m × 0.25mm I.D. × 0.25µm film thickness) with a 10m deactivated Integra-Guard™ guard column as the inlet. Sample volumes of 1 µL were injected. A selected-ion monitoring (SIM) program was constructed, in which quantifying ions and qualifying fragment ions (Table 4) were specified. FTOHs were separated into groups based on elution times (Table 5). Additional information regarding the analysis parameters is presented in Appendix 4. Typical mass chromatograms for a variety of sample types are depicted in Figure 2.

Eleven GC/MS analytes were investigated for their presence in the sludge-applied soils. Calibration curves were constructed using a mass-labeled matrix internal standard for all analytes, $^{2}H_2{}^{13}C_2$-10:2 FTOH (M10:2 FTOH). Commercial standards do not exist for some analytes, therefore these were quantified using standard curves for similar compounds in the homologous series. These analytes and the corresponding similar compound used for quantitation (shown in parentheses) are 9:2s FTOH (8:2 FTOH), 11:2s FTOH (10:2 FTOH), 12:2 FTOH (10:2 FTOH), 13:2s FTOH (10:2 FTOH) and 14:2 FTOH (10:2 FTOH) **(**Table 5). In the

absence of authentic standards, the identity of these compounds was tentatively identified by the loss of *m/*z 38 ($HF + H_2O$) from the $[M + 1]^+$ ion. The FTOH identities were then confirmed using trimethylsilylimidazole (TMSI) derivatization (Ellington et al., 2009). The limit of quantitation (LOQ) was determined using a signal/noise ratio (S/N>3) and the lowest acceptable standard concentration within ±30% of its theoretical value. The sample extract dilution factors are summarized in Table 1. The efficacy of the alcohols extractions was monitored using $^2H_2{}^{13}C_2$-8:2 FTOH (M8:2 FTOH) as a recovery internal standard. Soil concentration values for each analyte were calculated by multiplying the analyte concentration in the sample extract by the total volume of solvent extract, and then dividing the value by the soil dry weight (ng/g).

3. Quality Control

The sample analytical processes included prescribed quality control (QC) procedures to document data quality and analytical performance as defined in the ERD Quality Assurance Project Plan (March 26, 2009) and as noted below.

3.1 Field Blanks

Field blanks were used to check for contamination that might arise from any source in the study. Study field blanks consisted of commercially purchased Ottawa sand which has been documented to have low or no detectable levels of the targeted analytes (Washington et al., 2007; Ellington et al., 2009). Two field blanks were prepared by pouring the Ottawa sand into the cleaned HDPE soil sample containers, labeling the containers, and transporting the containers to and from the field without opening. Upon return to the laboratory, the field blanks were handled, extracted and analyzed exactly like all the soil samples. For field blanks, repeated extractions should fall within 15% of each other or be less than the method level of quantitation (LOQ).

3.2 Field Reference Soil

Field reference soils were used to check for artifacts in field sample handling or changes in the efficacy of extraction/analytical procedures. Field reference soil samples consisted of commercially purchased Cowart topsoil which has been documented to have moderate levels of several of the targeted analytes (Washington et al., 2007; Ellington et al., 2009). Two field reference soil samples were prepared by pouring the Cowart soil into the cleaned HDPE soil sample containers, labeling the containers, and transporting the containers to and from the field without opening). Upon return to the laboratory, the field reference soil samples were handled, extracted and analyzed exactly like all the soil samples. The precision of repeated extractions for the reference soil should fall within the acceptable quality-criterion range of ± 30%.

3.3 Field Duplicates

Duplicate soil samples provided a metric of the repeatability of the combined effects from heterogeneity of the distribution of analytes at the sampling scale in the field, variation in sampling or laboratory techniques, variation in sample containers or reagents, and/or analytical uncertainty. These data reflect the heterogeneity of the sample material in the field and provide a

measure of the reproducibility of results for samples collected with the objective of being morphologically and geographically identical at the field scale.

3.4 Background Field Samples

Background field soil samples served as a means for characterizing the local or regional soils PFC and/or FTOH contributions, if any. Background field sample values were compared with the land application area soil samples to characterize the extent and magnitude of PFC and FTOH contamination. Background soil samples were collected from an agricultural field (S101) where sludge was not applied. This background field was located near the sludge-treated fields. For background field samples, repeated extractions should fall within ±15% of each other or be less than the LOQ.

3.5 Laboratory Procedure Blanks

The full extraction procedure was performed in empty PPCO tubes identical to those used to extract the soil samples. These data should fall below the LOQ and are used to document that the extraction solvents and containers are free of the targeted analytes.

3.6 Laboratory Solvent Blanks

Laboratory solvent blanks, consisting of 60/40 ACN/H_2O, with and without matrix internal standards, were injected periodically during the sample runs. These data were used to demonstrate the eluents were free of the target analytes and that there was no sample "carry-over" from incomplete elution off the analytical column.

3.7 Laboratory Fortified Soil Extracts

Fortification of samples with target analytes provided data for verifying that the observed peaks are attributed correctly and that the quantitation is accurate. After initial LC/MS/MS analyses were completed, six samples were selected, split into a second pre-weighed autosampler vial, reweighed and fortified with a weighed amount of a standard. These fortified samples were then analyzed and the analytical concentrations compared to the theoretical concentrations, with the quality criterion being that measured values should fall within ± 30% of the calculated values**.**

3.8 GC/MS Identification of FTOHs in Soil Extracts

Targeted FTOH analytes were identified via GC/MS analysis using fragment ions and by the comparison to standards retention times (Figure 3). Both the GC/MS quantification ion and qualification ion were monitored for confirmation. Derivatizations with trimethylsilylimidazole (TMSI) were performed on selected samples to confirm the results and to ensure there were no interfering compounds and/or peaks (Figure 4).

3.9 Laboratory Recovery Internal Standards

Internal standards were used to document extraction recovery efficacy and the overall analytical accuracy. Known amounts of mass-labeled internal standards were added to all soil samples before extraction. Since mass-labeled recovery standards commonly contain small amounts of the unlabeled molecule, care was taken to avoid contaminating the samples with unlabeled analyte (Washington et al., 2007). Care was also taken to ensure the internal standards for the sample extracts requiring several-fold dilutions for calibration weren't diluted below the LOQ. The recovery internal standard added to LC/MS/MS analysis samples was $^{13}C_8$-labeled perfluorooctanoic acid ($^{13}C_8$-PFOA). The recovery internal standard added to GC/MS analysis samples was $^{2}H_2{}^{13}C_2$-8:2 FTOH. Using these internal standards, mean back-predicted values for all standards used to generate the calibration curves should fall within the acceptable quality criterion of ± 30% of the nominal values (Tables 6 and 7).

4. Results

4.1. Sample Completeness

All the surface soil and QC samples planned for this study were collected, analyzed, and reported (Table 8). A total of 30 sludge-applied soil samples were collected from the six fields where sludge had been applied. Four surface soil samples were collected at the background site. All the collected surface soil samples were analyzed for PFCs and FTOHs, and reported herein.

4.2. Standard Curve Back-Prediction

Tables 6 and 7 summarize the mean back-calculated values for the calibration curve standards for each PFC and FTOH, respectively. Mean back-calculated values for all standards above the LOQ are within the quality criterion of ± 30% of the calculated value, with the exception of the LC/MS/MS C14 985 pg/g standard. This deviation was determined to be associated with a laboratory mixing problem, and consequently was excluded from the C14 calibration.

4.3. Blank and Reference-Soil Samples Taken to the Field, and Background Fields

Tables 9 and 10 document the expected low to non-detect PFC and FTOH analyte levels for the QC sand and Cowart soil samples. For the sand blanks, analyte values all were less than the LOQ values (Tables 9 and 10). The precision of repeated extractions for the reference soil fell in the acceptable quality criterion range of ± 30% with the exceptions of C6, C14 and S4 (Tables 9 and 10), analytes falling at the outer limits of the homologues measured. These analytes have historically been among the most challenging analytes to measure. Analytical values for the reference soil fell in the same general ranges as previously detected (Washington et. al., 2007 and 2008a).

Tables 11 and 12 document the expected low to non-detect PFC and FTOH analyte levels for the background field samples. Most background sample analytes fell below the LOQs and the few detected analytes fell just above the LOQ. Out of the 23 low-level detections in these

background samples, four fell outside of the acceptable quality criterion for repeated extractions (± 15% of each other). These few non-compliances likely reflect the challenge of detecting values near the LOQ as well as heterogeneity in the sludge-applied soil samples.

4.4. Field Duplicates

Tables 13 and 14 summarize the field duplicate sample PFC and FTOH results (respectively) and associated percent relative difference (%RD). Duplicate sample results for the targeted acid species, PFOS, and the majority of the FTOH species are considered very good (<50% RD). Some of the duplicate sample results for 7:2s FTOH, 12:2 FTOH and 14:2 FTOH, however, exceeded the general range of other analytes, 50% RD. Consequently Table 14 includes within-sample FTOH results as well. The results of analysis on two extractions of the same sample yielded uniformly good results (<30%). Therefore, the high variability seen between different duplicate sample FTOH analytes most likely reflect true heterogeneity in the field samples.

4.5. Standard Addition and Precision of Analyses

The average recovery for the added concentration of PFC standards to the soils samples (Table 15) was within the acceptable range of ±30% of calculated values. The precision associated with two repeated injections of twelve FTOH sample extracts was <15% for all analytes (Table 16). These data confirm a satisfactory degree of analytical precision for both the acids and alcohols measured and reported for this study.

4.6 GC/MS Confirmation of FTOHs in Soil Extracts

Figure 3 shows the GC/MS technique for identifying 14:2 FTOH analyte using the qualifying fragmentation ions and the elution shift after TMSI derivatization. Figure 4 depicts the elution shift for the analytes, confirming their identities (e.g. the 8:2 FTOH peak disappears and the expected 8:2 FTOH derivative peak (–TMS replaces H) is detected in the TMSI treated extract).

4.7 Surface Soil Sample Results

Tables 17 and 18 summarize the results of analysis of the surface soil samples for the targeted PFCs and fluorotelomer alcohols, respectively. Soil PFOA concentrations ranged from 50-320 ng/g soil (ppb), two to three orders of magnitude above background (Table 11). Soil PFOS concentrations ranged from 30-410 ng/g soil (ppb), one to two orders of magnitude above background (Table 11). Generally the highest PFC mass concentrations were for PFDA (C10) and PFDoA (C12). For impacted soils, PFDA concentrations ranged from 130-990 ng/g (ppb) and PFDoA concentrations ranged from 30-530 ng/g (ppb), at least two orders of magnitude above the background field for both compounds. Of the S4-S8 sulfonates, only PFOS was detected. No unsaturated telomer acids were detected in the soil samples.

It is important to note the low recoveries for the Ottowa Sand field control samples. These samples are lower in organic carbon than all other samples in this study. The PMB 59.0

soil extraction procedure was developed with and for soils with higher organic carbon content. At this time, we suspect the loss of analytes arose during the cleanup step. Regardless, the analytical results for these low-recovery samples should be regarded as possibly lower than actually present in the soil. We plan to investigate the cause of these low recoveries and report more reliable values in the future.

Recovery of the internal FTOH standard was satisfactory for all samples (Table 1). All the fluorotelomer alcohols between 7:2s and 14:2 were detected in one or more samples. Soil 8:2FTOH concentrations ranged from 4 to ~90 ng/g (ppb), about one to two orders of magnitude above the background field values. The highest concentrations of FTOHs generally were 10:2FTOH and 12:2FTOH, which can degrade to PFDA and PFDoA, respectively. Impacted soils had 10:2FTOH concentrations ranging from 4-150 ng/g (ppb) and 12:2FTOH concentrations ranged from 2-160 ng/g (ppb), roughly one to three orders of magnitude above the background field sample levels (Table 10).

5. Discussion

These sample analysis results indicate that the majority of the Decatur soils in the land application area have concentrations of numerous PFCs and FTOHs above the background levels. In general, the highest mass-basis concentrations of the perfluorocarboxylic acids were the C8 through the C12 acids, particularly the even-chained C8, C10 and C12 acids; values commonly fell in the 100-800 ng/g range. Among the analyzed sulfonates, only PFOS was detected, with mass-basis concentrations falling in the same general range as the C8 through C12 carboxylic acids.

For the fluorotelomer alcohols in the land application areas, the 8:2 through the 12:2FTOHs generally measured at the highest concentrations; values commonly fell in the 10-100 ng/g range. In addition to measuring the commonly reported even-chained FTOHs (e.g., 8:2, 10:2, 12:2), the odd-chained secondary (sec) FTOHs (e.g., 7:2s, 9:2s, and 11:2s) were detected. Only the 7:2s-FTOH has been reported in peer-reviewed literature to our knowledge, and was interpreted as being a degradation product of 8:2FTOH (Ellington et. al., 2009a). Our working hypothesis is that these other FTOHs are degradation products of the respective homologues of 8:2FTOH.

A review of all the QC data reported for surface soil samples indicates highly satisfactory quality data (as defined by the quality criteria in the QAPP) for the samples for all analytes, carboxylic acids, sulfonates, and alcohols.

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Table 1: Sample Descriptions, Extract Dilutions & Internal Standard Recovery

Sample ID	Sample Description	Nominal Soil Dilution Ratio		Recovery Standard % Recovery (1)	
		LC/MS/MS	GC/MS	LC/MS/MS	GC/MS
S17-1aA	Surface composite	200	12	99	113
S17-1aAD	Duplicate	200	12	85	110
S17-1aB	Surface composite	200	12	84	113
S17-1aC	Surface composite	200	12	97	114
S17-1aD	Surface composite	200	12	79	113
S17-1aE	Surface composite	200	12	69	120
S1-4A	Surface composite	200	12	98	113
S1-4B	Surface composite	200	12	82	111
S1-4C	Surface composite	200	12	81	108
S1-4D	Surface composite	200	12	99	111
S1-4E	Surface composite	200	12	76	105
S1-4ED	Duplicate	200	12	105	107
S18-9A	Surface composite	200	12	86	111
S18-9B	Surface composite	200	12	112	109
S18-9C	Surface composite	200	12	109	107
S18-9D	Surface composite	200	12	86	94
S18-9E	Surface composite	200	12	59	118
S15-3A	Surface composite	200	12	102	107
S15-3B	Surface composite	200	12	110	109
S15-3C	Surface composite	200	12	87	115
S15-3D	Surface composite	200	12	87	113
S15-3E	Surface composite	200	12	80	112
S14-1A1	Surface grab	200	12	68	98
S14-10B1	Surface grab	200	12	111	101
S14-10C1	Surface grab	200	12	110	109
SALMG4A	Surface composite	1	12	102	103
Background Field Samples					
S101A1	Surface grab	1	12	71	116
S101B1	Surface composite	1	12	89	104
Field Quality Controls					
QC-1	Ottawa Sand	1	12	1	116
QC-2	Ottawa Sand	1	12	3	102
QC-3	Cowart Topsoil	1	12	99	113
QC-4	Cowart Topsoil	1	12	80	98

(1) Acceptable recovery is considered to be +/-30% of the ideal recovery of 100%.

Table 2: Liquid Chromatograph and Mass Spectrometer Parameters

Compound	Nominal Retention Time (RT) Apex RT (min)	Front RT (min)	Tail RT (min)	Delta T from Prev. Apex (min)	Number of Transitions	Number of Transitions Per Function	Parent Anion Mass (m/z)	Cone Potential (V)	Quan Ion Mass (m/z)	Quan Ion Collision Energy (eV)	Primary Qual Ion Mass (m/z)	Primary Qual Ion Collision Energy (eV)	2nd Qual Ion Mass (m/z)	2nd Qual Ion Collision Energy (eV)
Function 1 Time Interval 0 to 1.1 Min														
Perfluoropropanoic acid (C3)	0.65	0.4	0.9		2	5	162.80	14	118.80	11	69.80	25		
Perfluorobutanoic acid (C4)	0.70	0.4	1.0	0.05	1		212.85	13	168.80	10	Irregular response			
$^{3}C_{4}$-Perfluorobutanoic acid ((M+4)C4)	0.70	0.4	1.0	0.05	1		216.90	14	171.80	10	Irregular response			
Perfluoropentanoic acid (C5)	0.95	0.6	1.3	0.25	1		262.80	13	218.85	10	Irregular response			
Function 2 Time Interval 0.9 to 2.1 Min														
Perfluorohexanoic acid (C6)	1.35	1.0	1.7	**0.40**	2	7	312.80	13	268.85	10	118.80	20		
$^{3}C_{2}$-Perfluorohexanoic acid ((M+2)C6)	1.35	1.0	1.7	**0.40**	1		314.80	14	269.85	10	*119.30*	*20*		
Perfluorobutane sulfonate (PFBS)	1.50	1.2	1.8	0.15	2		298.90	40	79.85	30	98.85	40		
Perfluoroheptanoic acid (C7)	1.80	1.5	2.1	0.30	2		362.70	13	318.80	10	168.85	18		
Function 3 Time Interval 1.8 to 3.2 Min														
Perfluorooctanoic acid (C8)	2.30	1.9	2.7	**0.50**	2	11	412.70	14	368.75	10	168.85	18		
$^{3}C_{4}$-Perfluorooctanoic acid ((M+4)C8)	2.30	1.9	2.7	**0.50**	1		416.70	14	371.70	10	*171.85*	*18*		
$^{3}C_{8}$-Perfluorooctanoic acid ((M+8)C8)	2.30	1.9	2.7	**0.50**	1		420.70	13	375.70	11	*171.85*	*20*		
Perfluorohexane sulfonate (PFHxS)	2.50	2.1	2.9	0.20	2		398.90	50	79.85	40	98.85	40		
6:2 Fluorotelomer unsaturated acid (6:2FTUCA)	*2.60*	*2.2*	*3.0*	*0.10*	*1*		*357.00*	*16*	*293.00*	*17*				
$^{13}C_{2}$-6:2 Fluorotelomer unsaturated acid ((M+2)6:2FTUCA)	*2.60*	*2.2*	*3.0*	*0.10*	*1*		*359.00*	*16*	*294.00*	*17*				
Perfluorononanoic acid (C9)	2.75	2.4	3.1	0.15	2		462.70	15	418.70	11	218.85	18		
$^{13}C_{5}$-Perfluorononanoic acid ((M+5)C9)	2.75	2.4	3.1	0.15	1		467.70	15	422.70	12	*222.90*	*18*	*218.90*	*18*
Function 4 Time Interval 2.4 to 3.4 Min														
Perfluoroheptane sulfonate (PFHpS)	2.95	2.6	3.3	0.20	2	2	448.90	50	79.90	40	98.90	40		
Function 5 Time Interval 2.9 to 4.4 Min														
Perfluorodecanoic acid (C10)	3.35	3.0	3.7	**0.40**	2	11	512.90	15	468.70	11	218.85	20		
$^{13}C_{2}$-Perfluorodecanoic acid ((M+2)C10)	3.35	3.0	3.7	**0.40**	1		514.90	15	470.00	12				
Perfluorooctane sulfonate (PFOS)	3.55	3.2	3.9	0.20	2		498.90	60	79.85	50	98.85	40		
7:3 Fluorotelomer acid (7:3 FTCA)	*3.65*	*3.3*	*4.0*	*0.10*			*440.80*	*17*	*336.80*	*12*	*316.80*	*22*		
8:2 Fluorotelomer unsaturated acid (8:2FTUCA)	3.65	3.3	4.0	0.00	2		456.70	16	392.70	18	*342.70*	*40*		
$^{13}C_{2}$-8:2 Fluorotelomer unsaturated acid ((M+2)8:2FTUCA)	3.65	3.3	4.0	0.00	1		458.70	16	393.70	16	*343.70*	*40*		
Perfluoroundecanoic acid (C11)	3.90	3.6	4.2	0.25	2		562.70	15	518.70	12	218.85	20		
$^{13}C_{2}$-Perfluoroundecanoic acid ((M+2)C11)	3.90	3.6	4.2	0.25	1		564.90	15	520.00	13				
Function 6 Time Interval 4.0 to 15.0 Min														
Perfluorododecanoic acid (C12)	4.50	4.2	4.8	**0.60**	2	10	612.70	16	568.70	13	318.70	20		
$^{13}C_{2}$-Perfluorodecanoic acid ((M+2)C12)	4.50	4.2	4.8	**0.60**	1		614.90	16	570.00	13				
10:2 Fluorotelomer unsaturated acid (10:2FTUCA)	4.65	4.4	4.9	0.15	2		557.00	16	493.00	17	*443.00*	*38*		
$^{13}C_{2}$-10:2 Fluorotelomer unsaturated acid ((M+2)10:2FTUCA)	4.65	4.4	4.9	0.15	1		559.00	16	494.00	17				
Perfluorotridecanoic acid (C13)	5.15	4.9	5.4	0.50	2		662.75	16	618.70	13	318.70	22		
Perfluorotetradecanoic acid (C14)	5.80	5.5	6.1	0.65	2		712.75	18	668.70	14	318.70	24		

Italicized transitions are not monitored in 090428 MS Method
Most masses optimized by direct infusion on - 080707,8

Table 3: LC/MS/MS Integration and Optimization Parameters for Perfluorinated Chemicals Analysis

Compound	Savitzky Golay Smoothing # Points; # Smooths	Quan. Qual. Ratio & *Tolerance (%)*	Standards Range (pg/g) (# Levels)	Internal Standard	1/x-Weighted Calibration Equation	Correlation Coefficient (r^2)	Limit of Quantitation (pg/g)	Limit of Quantitation (LOQ) Definition
Function 1 Time Interval 0 to 1.1 Min								
Perfluoropronoic acid (C3)	5; 2							
Perfluorobutanoic acid (C4)	5; 2							
$^{13}C_4$-Perfluorobutanoic acid ((M+4)C4)	5; 2							
Perfluoropentanoic acid (C5)	0; 0							
Function 2 Time Interval 0.9 to 2.1 Min								
Perfluorohexanoic acid (C6)	5; 2	21. *+/- 44%*	0.9 - 4800 (14)	(M+2)C6	0.011*[pg/g] + 0.018	0.997	18	≥LOQ within 20% tolerance
$^{13}C_2$-Perfluorohexanoic acid ((M+2)C6)	5; 2		Invariant		Matrix Internal Standard			
Perfluorobutane sulfonate (PFBS)	5; 2	4.8 *+/- 44%*	9 - 4800 (12)	(M+2)C6	0.005*[pg/g] + 0.016	0.997	18	≥LOQ within 20% tolerance
Perfluoroheptanoic acid (C7)	0; 0	3.1 *+/- 44%*	5 - 4800 (13)	(M+4)C8	0.011*[pg/g] + 0.006	0.995	18	≥LOQ within 20% tolerance
Function 3 Time Interval 1.8 to 3.2 Min								
Perfluorooctanoic acid (C8)	5; 2	3.31 *+/- 44%*	0.9 - 4800 (14)	(M+4)C8	0.013*[pg/g] + 0.002	0.994	18	≥LOQ within 20% tolerance
$^{13}C_4$-Perfluorooctanoic acid ((M+4)C8)	5; 2		Invariant		Matrix Internal Standard			
$^{13}C_8$-Perfluorooctanoic acid ((M+8)C8)	5; 2		0.9 - 4800 (14)	(M+4)C8	0.013*[pg/g] + 0.002	0.997	5	LOQ within 30% tolerance, >LOQ within 20%
Perfluorohexane sulfonate (PFHxS)	5; 2	2.0 *+/- 44%*	5 - 4800 (13)	(M+4)C8	0.008*[pg/g] - 0.012	0.992	38	LOQ within 30% tolerance, >LOQ within 20%
6:2 Fluorotelomer unsaturated acid (6:2FTUCA)	5; 2			*(M+2)6:2FTUCA*				
$^{13}C_2$-6:2 Fluorotelomer unsaturated acid ((M+2)6:2FTUCA)	5; 2		Invariant		Matrix Internal Standard			
Perfluorononanoic acid (C9)	5; 2	4.3 *+/- 44%*	0.9 - 4800 (14)	(M+5)C9	0.011*[pg/g] + 0.015	0.996	18	≥LOQ within 20% tolerance
13C5-Perfluorononanoic acid ((M+5)C9)	5; 2		Invariant		Matrix Internal Standard			
Function 4 Time Interval 2.4 to 3.4 Min								
Perfluoroheptane sulfonate (PFHpS)	5; 2	1.5 *+/- 44%*	5 - 4800 (13)	(M+5)C9	0.003*[pg/g] + 0.002	0.973	56	≥LOQ within 30% tolerance
Function 5 Time Interval 2.9 to 4.4 Min								
Perfluorodecanoic acid (C10)	5; 2	6.8 *+/- 44%*	5 - 4800 (13)	(M+2)C10	0.011*[pg/g] + 0.016	0.992	18	≥LOQ within 20% tolerance
$^{13}C_2$-Perfluorodecanoic acid ((M+2)C10)	5; 2		Invariant		Matrix Internal Standard			
Perfluorooctane sulfonate (PFOS)	5; 2	1.32 *+/- 44%*	5 - 4800 (12)	(M+2)C10	0.004*[pg/g] + 0.003	0.990	38	≥LOQ within 20% tolerance
7:3 Fluorotelomer acid (7:3 FTCA)	5; 2							
8:2 Fluorotelomer unsaturated acid (8:2FTUCA)	5; 2		5 - 4800 (13)	(M+2)8:2FTUCA	0.010*[pg/g] + 0.005	0.992	18	≥LOQ within 20% tolerance
$^{13}C_2$-8:2 Fluorotelomer unsaturated acid ((M+2)8:2FTUCA)	5; 2		Invariant		Matrix Internal Standard			
Perfluoroundecanoic acid (C11)	5; 2	8.8 *+/- 44%*	5 - 4800 (13)	(M+2)C11	-2.66e-7*[pg/g]^2 + 0.010*[pg/g] - 0.010	0.997	18	≥LOQ within 20% tolerance
$^{13}C_2$-Perfluoroundecanoic acid ((M+2)C11)	5; 2		Invariant		Matrix Internal Standard			
Function 6 Time Interval 4.0 to 15.0 Min	5; 2							
Perfluorododecanoic acid (C12)	5; 2	10.8 *+/- 44%*	0.9 - 4800 (14)	(M+2)C12	-7.54e-7*[pg/g]^2+ 0.010*[pg/g] + 0.006	0.998	38	≥LOQ within 20% tolerance
$^{13}C_2$-Perfluorodecanoic acid ((M+2)C12)	5; 2		Invariant		Matrix Internal Standard			
10:2 Fluorotelomer unsaturated acid (10:2FTUCA)	5; 2		0.9 - 4800 (14)	(M+2)10:2FTUCA	0.010*[pg/g] + 0.006	0.991	18	≥LOQ within 20% tolerance
$^{13}C_2$-10:2 Fluorotelomer unsaturated acid ((M+2)10:2FTUCA)	5; 2		Invariant		Matrix Internal Standard			
Perfluorotridecanoic acid (C13)	5; 2	12.9 *+/- 44%*	5 - 4800 (13)	(M+2)C12	-8.86e-7*[pg/g]^2 + 0.013*[pg/g] + 0.033	0.997	18	≥LOQ within 20% tolerance
Perfluorotetradecanoic acid (C14)	5; 2	16.9 *+/- 44%*	5 - 4800 (13)	(M+2)C12	-9.72e-7*[pg/g]^2 + 0.013*[pg/g] + 0.002	0.996	18	≥LOQ within 20% tolerance

Table 4: Gas Chromatograph/Mass Spectrometer Parameters for Fluorotelomer Alcohols Analysis

Compound of Interest	Formula & Molecular Weight	Acronym	Ions in PCI[1] (m/z)	Ions in NCI[2] (m/z)	PCI TMSI Derivatives[1,3] (m/z)
1H,1H,2H,2H-perfluorooctan-1-ol	$CF_3(CF_2)_5CH_2$-CH_2-OH 364	6:2 FTOH	365[*4], 327	304, 284	437
1H,1H,2H,2H-perfluorodecan-1-ol	$CF_3(CF_2)_7CH_2$-CH_2-OH 464	8:2 FTOH	465[*], 427	404, 384	537
$1^2H,1^2H,2H,2H$-$^{13}C_2$-perfluorodecan-1-ol	$CF_3(CF_2)_7{}^{13}CH_2$-$^{13}CD_2$-OH 468	M8:2 FTOH	469[*],431		
1H,1H,2H,2H-perfluorododecan-1-ol	$CF_3(CF_2)_9CH_2$-CH_2-OH 564	10:2 FTOH	565[*], 527	504,484	637
$1^2H,1^2H,2H,2H$-$^{13}C_2$-perfluorododecan-1-ol	$CF_3(CF_2)_9{}^{13}CH_2$-$^{13}CD_2$-OH 568	M10:2 FTOH	569[*], 531		
1H,1H,2H,2H-perfluorotetradecan-1-ol	$CF_3(CF_2)_{11}CH_2$-CH_2-OH 664	12:2 FTOH	665, 627		737
1H,1H,2H,2H-perfluorohexadecan-1-ol	$CF_3(CF_2)_{13}CH_2$-CH_2-OH 764	14:2 FTOH	765, 727		837
1-Perfluoroheptylethanol	$[CF_3(CF_2)_6](CH_3)$-CH-OH	7:2 sFTOH	415, 395, 377		487
1-Perfluorononylethanol	$[CF_3(CF_2)_8](CH_3)$-CH-OH	9:2 sFTOH	615, 577		687
1-Perfluoroundecylethanol	$[CF_3(CF_2)_{10}](CH_3)$-CH-OH	11:2 sFTOH	715, 677		787
1-Perfluorotridecylethanol	$[CF_3(CF_2)_{12}](CH_3)$-CH-OH	13:2 sFTOH	815, 777		887
2-(Perfluorooctyl) ethyl acrylate	$F(CF_2)_8CH_2$-CH_2-O-C(O)CH=CH_2	8:2 FT-acrylate	519		
1H,1H-perfluoroundecan-1-ol	$CF_3(CF_2)_9CH_2$-OH 550	10:1 FTOH	551, 531		623

1. Positive Chemical Ionization
2. Negative Chemical Ionization
3. Extracts were treated with trimethylsilylimidazole
4. Asterisk denotes the principal ion for quantitation

Table 5. GC-MS Integration and Optimization Parameters for Fluorotelomer Alcohols Analysis

Compound	Apex RT	Cycles /Sec	Standard Range (pg/mL)	Matrix Internal Standard	Equal-weighted calibration equation	Correlation Coefficient (r^2)	Limit of Quantitation (ng/g dry soil)[2)]
Group 1 : Time Interval 4.5 to 8.5 min							
6:2 FTOH	7.986	2.37	200 – 5000 (4)	M10:2 FTOH	2.57×[pg/mL]	0.999	2.4
7:2s FTOH	8.133		200 – 5000 (4)	M10:2 FTOH	1.75×[pg/mL]	0.999	2.6
Group 2 : Time Interval 8.5 to 9.6 min							
M8:2 FTOH	9.239	1.21	100 – 5000 (5)	M10:2 FTOH	1.56×[pg/mL]	0.999	0.9
8:2 FTOH	9.256		100 – 5000 (5)	M10:2 FTOH	1.79×[pg/mL]	0.999	0.9
6:2 FT-acrylate	9.380		N.A.[1)] (8:2 FT-acrylate)	M10:2 FTOH	2.45×[pg/mL]	0.999	0.9
9:2s FTOH	9.356		N.A. (8:2 FTOH)	M10:2 FTOH	1.79×[pg/mL]	0.999	0.9
Group 3 : Time Interval 9.6 to 10.6 min							
10:1 FTOH	9.758	0.98	200 – 5000 (4)	M10:2 FTOH	3.86×[pg/mL]	0.999	2.4
M10:2 FTOH	10.187		Invariant	-	Invariant	-	-
10:2 FTOH	10.207		200 – 5000 (4)	M10:2 FTOH	8.24×[pg/mL]	0.999	2.4
8:2 FT-acrylate	10.248		100 – 5000 (5)	M10:2 FTOH	2.45×[pg/mL]	0.999	0.9
11:2s FTOH	10.243		N.A. (10:2 FTOH)	M10:2 FTOH	1.75×[pg/mL]	0.999	2.4
Group 4 : Time Interval 10.6 to 12.4 min							
12:2 FTOH	10.973	1.21	N.A. (10:2 FTOH)	M10:2 FTOH	2.45×[pg/mL]	0.999	2.4
13:2s FTOH	10.959		N.A. (10:2 FTOH)	M10:2 FTOH	2.45×[pg/mL]	0.999	2.4
14:2 FTOH	11.580		N.A. (10:2 FTOH)	M10:2 FTOH	2.45×[pg/mL]	0.999	2.4
10:2 FT-acrylate	11.740		N.A. (8:2 FT-acrylate)	M10:2 FTOH	2.45×[pg/mL]	0.999	2.4

1) An analyte whose genuine standard was not available (N.A.), we quantified it using standard curve for similar compound in the homologous series.

2) Limit of Quantitation (LOQ) was defined as signal/noise ratio (S/N>3) and the lowest standard within ±30% of its theoretical value then multiplying by the average sample-dilution factors.

Table 6: Percent Deviation of Mean Back-Predicted Values for Perfluorinated Chemical Standard Curve Points [1]

Std Value pg/g	C6	C7	C8	M8C8	C9	C10	C11	C12	C13	C14	S4	S6	S7	S8	U8:2	U10:2
0.9	**-56.2**	**ND**	9.5	26.0	**327**	**ND**	**524**	**31.4**	**53.5**	**ND**	**ND**	**ND**	**ND**	**ND**	-23.2	**-53.4**
4.5	6.7	-12.2	-19.9	-2.2	**-45.9**	**-32.5**	16.7	-13.3	**-43.7**	-4.4	**-40.0**	13.0	-3.5	16.2	0.1	9.4
9.2	-20.2	-3.4	-8.8	-9.9	**-31.6**	2.8	16.2	-12.8	-14.9	10.0	4.2	12.5	12.2	3.8	10.7	13.5
18.1	5.7	-6.7	-11.4	-4.0	-5.9	3.0	-0.1	8.2	1.2	2.2	4.2	-3.4	4.7	0.8	3.1	17.8
38.0	-2.0	0.2	-4.6	-0.9	4.6	-4.3	-5.8	-1.9	0.8	0.1	1.9	2.0	12.5	-5.9	4.5	6.7
55.7	2.4	9.0	-0.9	-1.9	-3.7	1.2	-1.9	-3.6	2.5	0.8	-1.6	6.8	7.3	-9.3	-0.6	12.3
72.8	0.4	18.0	5.6	5.9	1.0	5.1	-5.4	2.9	-1.6	-14.1	-2.1	-3.3	2.4	8.0	2.9	11.4
92.9	2.6	0.4	0.9	-0.9	-2.4	1.8	-2.7	1.3	5.6	4.4	-2.0	-5.0	9.8	-12.3	4.1	5.8
231.2	2.3	8.7	7.2	0.9	-1.6	9.4	-1.4	4.3	5.7	6.8	0.9	-3.6	3.6	-5.3	8.5	6.2
483.3	4.0	2.9	2.0	1.8	0.7	5.1	0.3	1.9	4.1	2.0	3.4	0.4	1.9	-2.1	1.1	5.4
720.1	1.4	7.0	-3.3	7.0	-8.6	6.0	-1.3	-1.7	1.4	-2.1	0.8	-7.8	-5.5	1.2	-2.6	-2.1
985.0	13.4	-12.1	18.4	2.8	-9.5	6.6	2.9	0.2	-9.5	**-31.9**	7.8	-9.8	-13.4	3.3	8.3	5.8
2377	-1.4	4.6	-1.6	-0.9	5.6	-2.6	0.2	-0.7	3.2	-0.1	-2.1	-4.9	9.6	-12.3	-2.8	5.1
4757	-1.3	-0.5	-2.8	-1.1	0.9	-1.7	0.1	1.2	-0.1	1.8	-1.0	5.1	-0.9	0.0	-1.2	-4.7

[1] Bold values do not meet the quality criterion of being within 30% of the nominal standard concentration. With exception of the 985 pg/g value for C14, the emboldened values are the highest standard concentration that falls below the limit of quantitation. The 985 pg/g C14 standard was omitted from the standard curve, see text for details.

Table 7: Percent Deviation of Mean Back-Predicted Values for Fluorotelomer Alcohols Standard Curve Points

Std Value (pg/mL)	6:2 FTOH	7:2s FTOH	M8:2 FTOH	8:2 FTOH	10:1 FTOH	10:2 FTOH	8:2 FT-Acryl.
116	-17.3	-28.7	-13.3	3.4	-15.2	-11.2	-8.7
297	-18.7	-7.6	-2.2	-4.2	-5.8	-7.4	0.0
610	-18.1	2.4	-16.3	-13.1	-11.6	-8.7	-6.3
1205	-5.8	-8.9	-8.0	-4.9	-12.3	-10.3	-7.7
6085	3.8	4.0	3.7	3.5	4.1	3.6	3.6

Table 8: Proposed, Collected and Analyzed Samples Documenting Completeness

Sample Type	Planned	Collected	Analyzed	
			LC/MS/MS	GC/MS
Sludge-Applied Field Samples	30	30	30	30
Background Field Samples	4	4	4	4
Field Duplicates	2	2	2	2
Field Blanks	2	2	2	2
Field Reference Soil Samples	2	2	2	2
Laboratory Extract Spikes	5	5	5	0

Table 9. Summary of Field Blanks and QC Soil (pg/g dry soil) for Perfluorinated Chemical Analysis

Sample Type	C6	C7	C8	M8C8*	C9	C10	C11	C12	C13	C14	S4	S6	S7	S8	U8:2	U10:2
**Field Blanks	<LOQ	<LOQ	<LOQ	*27*	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Field Blank (SD)				*18.6*												
% Precision (RSD)				69												
*QC Soils	*147*	105	363	3271	114	153	114	110	41	*23*	*55*	71	<LOQ	1532	<LOQ	<LOQ
QC Soils, SD	*33.8*	7.0	47.0	477.4	17.3	16.2	12.8	5.6	3.4	*16.2*	*65.5*	7.5		28.5		
% Precision (RSD)	*23*	7	13	15	15	11	11	5	8	*71*	*120*	11		2		

*M8C8 is an internal standard

**Mean of 4 determinations. QC Soil is Cowart, previously analyzed in multiple studies

NA designates 'not applicable' because the target analyte was not detected

Italicized values fall outside acceptable tolerance of 15% for repeated extractions, but are reported for completeness

Table 10. Summary of Field Blanks and QC Soil (ng/g dry soil) for Fluorotelomer Alcohol Analysis

Sample Type	6:2 FTOH	7:2s FTOH	8:2 FTOH	9:2s FTOH	10:2 FTOH	11:2s FTOH	8:2 FT-acrylate	12:2 FTOH	13:2s FTOH	14:2 FTOH	% M8:2 Rec.[2)]
Sand	< 2.4[1)]	< 2.6	< 0.9	< 0.9	< 2.4	< 2.4	< 0.9	< 2.4	< 2.4	< 2.4	109
Cowart Soil	< 2.4	< 2.6	< 0.9	< 0.9	< 2.4	< 2.4	< 0.9	< 2.4	< 2.4	< 2.4	105

1) Mean values of two replicated extractions were less than its respective Limit of Quantitation
2) Mass-labeled 8:2 FTOH was spiked before an extraction to monitor overall extraction efficiencies.

Table 11. Summary of Background Field Soils (pg/g dry soil) for Perfluorinated Chemical Analysis

																% Rec'y
Sample ID	**C6**	**C7**	**C8**	**C9**	**C10**	**C11**	**C12**	**C13**	**C14**	**S4**	**S6**	**S7**	**S8**	**U8:2**	**U10:2**	**M8C8**
S101A1	<LOQ	0.03	0.17	0.08	0.05	0.04	<LOQ	<LOQ	<LOQ	0.09	<LOQ	<LOQ	1.90	<LOQ	<LOQ	71
		0.01	*0.02*	*0.03*	*0.01*	*0.05*				*0.03*			*0.30*			*33*
S101A2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.12	0.06	<LOQ	0.05	<LOQ	<LOQ	18
										0.02	0.00		*0.02*			*2*
S101B1	0.02	0.04	0.21	0.05	<LOQ	0.03	<LOQ	<LOQ	<LOQ	0.06	<LOQ	<LOQ	1.25	<LOQ	<LOQ	89
	0.02	*0.00*	*0.03*	*0.01*		*0.00*				*0.03*			*0.01*			*1*
S101B2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.14	0.07	<LOQ	0.16	<LOQ	<LOQ	6
										0.03	*0.00*		*0.08*			*1*

*M8C8 is an internal standard

Table 12. Summary of Background Field Soils (ng/g dry soil) for Fluorotelomer Alcohol Analysis

Sample ID		6:2 FTOH	7:2s FTOH	8:2 FTOH	9:2s FTOH	10:2 FTOH	11:2s FTOH	8:2 FT-acrylate	12:2 FTOH	13:2s FTOH	14:2 FTOH	% M8:2* Rec.
S101A1	Mean	< 2.4	< 2.6	< 0.9	< 0.9	< 2.4	< 2.4	< 0.9	< 2.4	< 2.4	< 2.4	116.1
	% RD	-	-	-	-	-	-	-	-	-	-	*2*
S101A2	Mean	< 2.4	< 2.6	< 0.9	< 0.9	< 2.4	< 2.4	< 0.9	< 2.4	< 2.4	< 2.4	119.5
	% RD	-	-	-	-	-	-	-	-	-	-	*9*
S101B1	Mean	< 2.4	< 2.6	< 0.9	< 0.9	< 2.4	< 2.4	< 0.9	< 2.4	< 2.4	< 2.4	104.4
	% RD	-	-	-	-	-	-	-	-	-	-	*9*
S101B2	Mean	< 2.4	< 2.6	< 0.9	< 0.9	< 2.4	< 2.4	< 0.9	< 2.4	< 2.4	< 2.4	103.6
	% RD	-	-	-	-	-	-	-	-	-	-	*12*

*Mass-labeled 8:2 FTOH was spiked before an extraction to monitor overall extraction efficiencies.

Table 13. Summary of Duplicate Field Samples (ng/g dry soil) for Perfluorinated Chemical Analysis

Sample ID	C6	C7	C8	M8C8*	C9	C10	C11	C12	C13	C14	S4	S6	S7	S8	U8:2	U10:2
090326-S17-1aA	19	38	190	4	91	684	199	396	65	70	1	1	2	127	0	1
0903261-S17-1aAD	27	53	269	4	132	986	233	526	81	114	0	3	0	189	0	1
Rel % Diff	35	35	34	11	37	36	16	28	21	48	NA	117	NA	39	NA	NA
09032-S1-4E-4	7	30	153	5	76	509	133	245	40	52	0	4	1	177	0	0
090326-S1-4ED-4	11	49	264	7	110	683	171	349	61	90	0	4	0	245	0	1
Rel % Diff	38	47	53	23	37	29	25	35	41	53		9	NA	32		200

*M8C8 is an internal standard

Table 14. Summary of Duplicate Field Samples (ng/g dry soil) for Fluorotelomer Alcohols Analysis

Sample ID		6:2 FTOH	7:2s FTOH	8:2 FTOH	9:2s FTOH	10:2 FTOH	11:2s FTOH	8:2 FT-acrylate	12:2 FTOH	13:2s FTOH	14:2 FTOH	% Rec.[2)]
S17-1aA	Sub-mean	< 2.4 [1)]	28.7	49.5	16.8	56.0	13.4	< 0.9	31.5	4.4	31.5	113.0
	% RD	-	3.6	17.6	22.1	14.7	17.7	-	27.1	3.9	12.8	3.3
S17-1aA-Duplicate	Sub-mean	< 2.4	43.1	80.1	25.0	95.8	20.5	1.0	50.3	6.9	52.4	109.6
	% RD	-	0.4	16.9	4.5	18.6	4.3	-	3.3	12.1	9.6	0.6
	Mean	< 2.4	35.9	64.8	20.9	75.9	17.0	< 0.9	40.9	5.7	41.9	111.3
	% RD	-	40.3	47.3	38.9	52.5	41.4	-	45.9	43.4	49.8	3.1
S1-4E	Sub-mean	< 2.4	12.7	27.7	9.0	30.8	4.5	< 0.9	10.9	< 2.4	10.2	107.4
	% RD	-	2.6	9.2	26.5	23.2	12.6	-	18.0	-	2.1	0.6
S1-4E-Duplicate	Sub-mean	< 2.4	27.8	42.7	16.2	52.1	9.6	< 0.9	21.8	3.3	26.3	109.6
	% RD	-	1.1	5.6	6.4	1.9	13.5	-	0.2	13.4	0.6	2.9
	Mean	< 2.4	20.3	35.2	12.6	41.5	7.1	< 0.9	16.4	-	18.3	108.5
	% RD	-	74.3	42.7	57.3	51.5	72.5	-	66.9	-	88.1	2.1

1) Mean values of two replicated extractions were less than its respective Limit of Quantitation

2) Mass-labeled 8:2 FTOH was spiked before an extraction to monitor overall extraction efficiencies.

Table 15. Standard Addition of 100pg of Perfluorinated Chemicals to Selected Field Samples

Sample ID	pg C6	pg C7	pg C8	pg M8C8	pg C9	pg C10	pg C11	pg C12	pg C13	pg C14	pg S4	pg S6	pg S7	pg S8	pg U8	pg U10
	LCMSMS Analyzed Added Mass of Analyte															
S14-1A1-SA	111	104	106	104	78	113	95	111	135	136	113	100	124	167	109	116
S14-1A2-SA	118	116	106	105	118	135	107	103	116	124	119	109	142	119	114	112
S14-1A3-SA	117	99	111	107	96	107	98	115	116	114	115	109	111	98	107	131
S14-10B1-SA	115	115	127	109	93	124	84	90	109	115	103	121	119	116	109	93
S14-10C1-SA	107	131	146	116	101	167	65	115	142	130	131	109	127	189	118	109
	Actual Added Mass of Analyte															
	pg C6	**pg C7**	**pg C8**	**pg M8C8**	**pg C9**	**pg C10**	**pg C11**	**pg C12**	**pg C13**	**pg C14**	**pg S4**	**pg S6**	**pg S7**	**pg S8**	**pg U8**	**pg U10**
S14-1A1-SA	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104
S14-1A2-SA	107	107	107	107	107	107	107	107	106	106	106	106	106	106	106	106
S14-1A3-SA	109	109	109	109	109	109	109	109	108	108	108	108	108	108	108	108
S14-10B1-SA	107	107	107	107	107	107	107	107	107	107	107	107	107	107	107	107
S14-10C1-SA	107	107	107	107	107	107	107	107	107	107	107	107	107	107	107	107
	Percent Recovery of Added Analyte via LCMSMS Analysis															
	C6	**C7**	**C8**	**M8C8**	**C9**	**C10**	**C11**	**C12**	**C13**	**C14**	**S4**	**S6**	**S7**	**S8**	**U8**	**U10**
S14-1A1-SA	107	100	102	100	75	108	92	106	130	131	109	96	119	161	105	112
S14-1A2-SA	111	109	99	99	111	127	100	97	109	116	111	102	134	112	107	105
S14-1A3-SA	108	91	102	99	88	99	90	106	107	105	106	100	102	90	98	120
S14-10B1-SA	107	107	118	102	87	116	79	84	102	108	96	113	112	109	102	88
S14-10C1-SA	100	122	136	108	95	156	61	108	133	121	122	102	119	177	111	102
Avg % Rec'y	107	106	112	102	91	121	84	100	116	116	109	103	117	130	105	105
SD % Rec'y	4.0	11.6	15.8	4.0	13.0	21.9	15.1	9.9	14.4	10.5	9.4	6.3	11.6	37.2	4.6	12.2

SA = Standard Addition of 50uL of 2500 pg/g mix of each analyte to 500uL of 200X diluted sample, which is equivalent to 100pg increment.
Values below LOQ assumed to be zero for calculation purposes.

Table 16. Precision of Repeated Injections for Fluorotelomer Alcohols (n=12)

Compound	6:2 FTOH	7:2s FTOH	8:2 FTOH	9:2s FTOH	10:2 FTOH	11:2s FTOH	8:2 FT-acrylate	12:2 FTOH	13:2s FTOH	14:2 FTOH	M8:2 FTOH
Mean % RD[1)]	- [2)]	7.0	9.5	10.0	10.6	13.8	-	15.5	23.3	14.5	5.7
s.d. (%)	-	5.8	4.2	6.7	7.9	10.5	-	5.8	14.2	7.1	4.7

1) Selected samples (n=12) were injected twice to evaluate the precision of GC/MS performance. The % RD (% relative difference) was calculated for each extract and, subsequently, mean and standard deviation (s.d.) were reported.
2) Values were less than its respective Limit of Detection.

Table 17. Concentrations of Perfluorinated Acids and Sulfonates in Surface Soils from Decatur, AL (ng/g dry soil)*

Sample ID	C6	C7	C8	C9	C10	C11	C12	C13	C14	S4	S6	S7	S8	U8:2	U10:2
S17-1aA	19	38	190	91	684	199	396	65	70	<LOQ	<LOQ	<LOQ	127	<LOQ	<LOQ
S17-1aAD	27	53	269	132	986	233	526	81	114	<LOQ	<LOQ	<LOQ	189	<LOQ	<LOQ
S17-1aB	<LOQ	21	120	67	420	138	240	41	51	<LOQ	<LOQ	<LOQ	81	<LOQ	<LOQ
S17-1aC	26	50	249	104	614	146	257	40	36	<LOQ	<LOQ	<LOQ	122	<LOQ	<LOQ
S17-1aD	<LOQ	19	87	49	323	104	174	33	19	<LOQ	<LOQ	<LOQ	58	<LOQ	<LOQ
S17-1aE	16	28	139	73	405	108	239	38	63	<LOQ	<LOQ	<LOQ	73	<LOQ	<LOQ
S1-4A	35	80	312	118	528	126	179	27	32	<LOQ	<LOQ	<LOQ	203	<LOQ	<LOQ
S1-4B	12	42	233	115	562	146	206	34	47	<LOQ	<LOQ	<LOQ	164	<LOQ	<LOQ
S1-4C	20	39	183	90	566	154	304	54	79	<LOQ	<LOQ	<LOQ	202	<LOQ	<LOQ
S1-4D	24	51	255	137	830	311	498	75	135	<LOQ	<LOQ	<LOQ	325	<LOQ	<LOQ
S1-4E	<LOQ	30	153	76	509	133	245	40	52	<LOQ	<LOQ	<LOQ	177	<LOQ	<LOQ
S1-4ED	11	49	264	110	683	171	349	61	90	<LOQ	<LOQ	<LOQ	245	<LOQ	<LOQ
S18-9A	<LOQ	17	94	58	353	139	215	37	49	<LOQ	<LOQ	<LOQ	118	<LOQ	<LOQ
S18-9B	12	21	133	95	557	238	407	70	82	<LOQ	<LOQ	<LOQ	160	<LOQ	<LOQ
S18-9C	<LOQ	14	119	82	277	101	158	25	26	<LOQ	<LOQ	<LOQ	88	<LOQ	<LOQ
S18-9D	<LOQ	16	123	89	414	142	261	46	76	<LOQ	<LOQ	<LOQ	99	<LOQ	<LOQ
S18-9E	<LOQ	7	54	34	163	58	92	16	24	<LOQ	<LOQ	<LOQ	61	<LOQ	<LOQ
S15-3A	<LOQ	16	105	34	132	21	30	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	35	<LOQ	<LOQ
S15-3B	<LOQ	11	64	26	141	26	35	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	31	<LOQ	<LOQ
S15-3C	<LOQ	13	87	47	231	29	34	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	36	<LOQ	<LOQ
S15-3D	17	31	185	67	343	44	71	10	19	<LOQ	<LOQ	<LOQ	82	<LOQ	<LOQ
S15-3E	19	41	236	93	445	62	92	12	21	<LOQ	<LOQ	<LOQ	82	<LOQ	<LOQ
S14-1A1	<LOQ	14	84	83	419	126	186	36	34	<LOQ	<LOQ	<LOQ	203	<LOQ	<LOQ
S14-10B1	<LOQ	11	60	39	349	171	341	66	65	<LOQ	<LOQ	<LOQ	149	<LOQ	<LOQ
S14-10C1	28	61	317	129	670	279	293	68	49	<LOQ	<LOQ	<LOQ	408	<LOQ	<LOQ
SALMG4a	<LOQ	<LOQ	0.17	0.06	0.12	0.07	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	4.5	<LOQ	<LOQ

*Mean values of two replicated extractions; LOQ = Limit of Quantization

Field S14 is Chuck Simmons Farm (info from C. Simmons)

Table 18. Concentrations of Fluorotelomer Alcohols in Surface Soil Samples from Decatur, AL (ng/g dry soil)*

Sample ID	6:2 FTOH	7:2s FTOH	8:2 FTOH	9:2s FTOH	10:2 FTOH	11:2s FTOH	8:2 FT-acrylate	12:2 FTOH	13:2s FTOH	14:2 FTOH
S17-1aA	< 2.4	28.7	49.5	16.8	56.0	13.4	< 0.9	31.5	4.4	31.5
S17-1aA Dup	< 2.4	43.1	80.1	25.0	95.8	20.5	1.0	50.3	6.9	52.4
S17-1aB	< 2.4	15.7	22.4	8.4	24.9	8.3	< 0.9	16.5	3.6	20.7
S17-1aC	< 2.4	36.5	73.2	16.0	70.3	9.6	< 0.9	35.1	< 2.4	22.9
S17-1aD	< 2.4	11.1	19.6	7.2	20.5	5.4	< 0.9	11.2	< 2.4	12.4
S17-1aE	< 2.4	19.5	44.6	12.7	38.7	9.2	< 0.9	19.1	3.2	21.3
S1-4A	< 2.4	19.0	33.0	14.6	44.7	6.1	< 0.9	17.9	2.4	16.2
S1-4B	< 2.4	8.9	30.1	7.8	41.5	6.3	< 0.9	22.5	2.6	18.6
S1-4C	< 2.4	15.2	34.2	9.6	31.1	7.7	< 0.9	14.8	3.0	18.5
S1-4D	< 2.4	22.1	53.5	14.0	77.2	12.9	< 0.9	47.7	5.9	50.5
S1-4E	< 2.4	12.7	27.7	9.0	30.8	4.5	< 0.9	10.9	< 2.4	10.2
S1-4E Dup	< 2.4	27.8	42.7	16.2	52.1	9.6	0.5	21.8	3.3	26.3
S18-9A	< 2.4	5.4	14.7	5.5	13.9	7.5	< 0.9	8.8	2.7	12.9
S18-9B	< 2.4	13.2	20.9	9.2	26.3	7.4	< 0.9	14.0	4.3	15.5
S18-9C	< 2.4	< 2.6	4.8	2.0	4.6	3.7	< 0.9	3.6	< 2.4	5.4
S18-9D	< 2.4	6.2	12.7	6.6	11.6	8.8	< 0.9	9.5	4.0	14.6
S18-9E	< 2.4	< 2.6	4.9	1.8	4.2	< 0.9	< 0.9	< 2.4	< 2.4	3.3
S15-3A	< 2.4	4.5	11.2	3.1	17.0	2.6	< 0.9	9.2	< 2.4	6.2
S15-3B	< 2.4	8.4	21.3	5.8	23.2	3.7	< 0.9	14.7	< 2.4	9.0
S15-3C	< 2.4	7.1	18.0	2.9	20.2	< 0.9	< 0.9	7.2	< 2.4	4.0
S15-3D	< 2.4	16.8	36.3	15.1	64.9	10.3	< 0.9	54.2	< 2.4	23.8
S15-3E	< 2.4	19.5	61.5	24.0	150.0	13.6	< 0.9	133.7	< 2.4	53.7
S14-1A1	< 2.4	7.3	11.1	4.5	10.9	5.1	< 0.9	7.2	1.4	9.9
SALMG4A	< 2.4	< 2.6	< 0.9	< 0.9	< 2.4	3.0	< 0.9	< 2.4	< 2.4	< 2.4

*Mean values of two replicated extractions

Figure 1.a. Chromatograms for Perfluorocarboxylic Acids

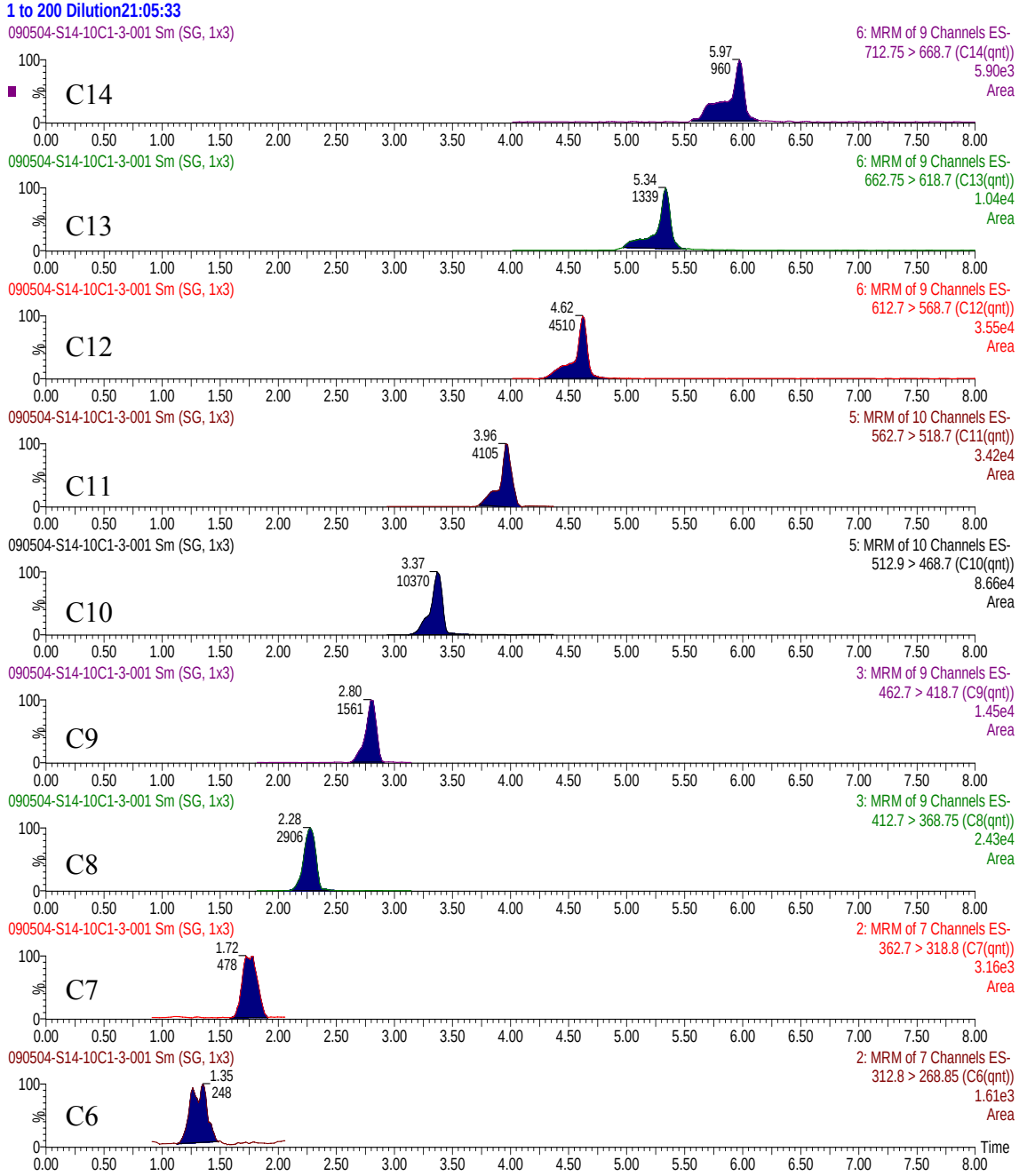


Figure 1.b. Chromatograms for Perfluorosulfonates and Unsaturated Acids

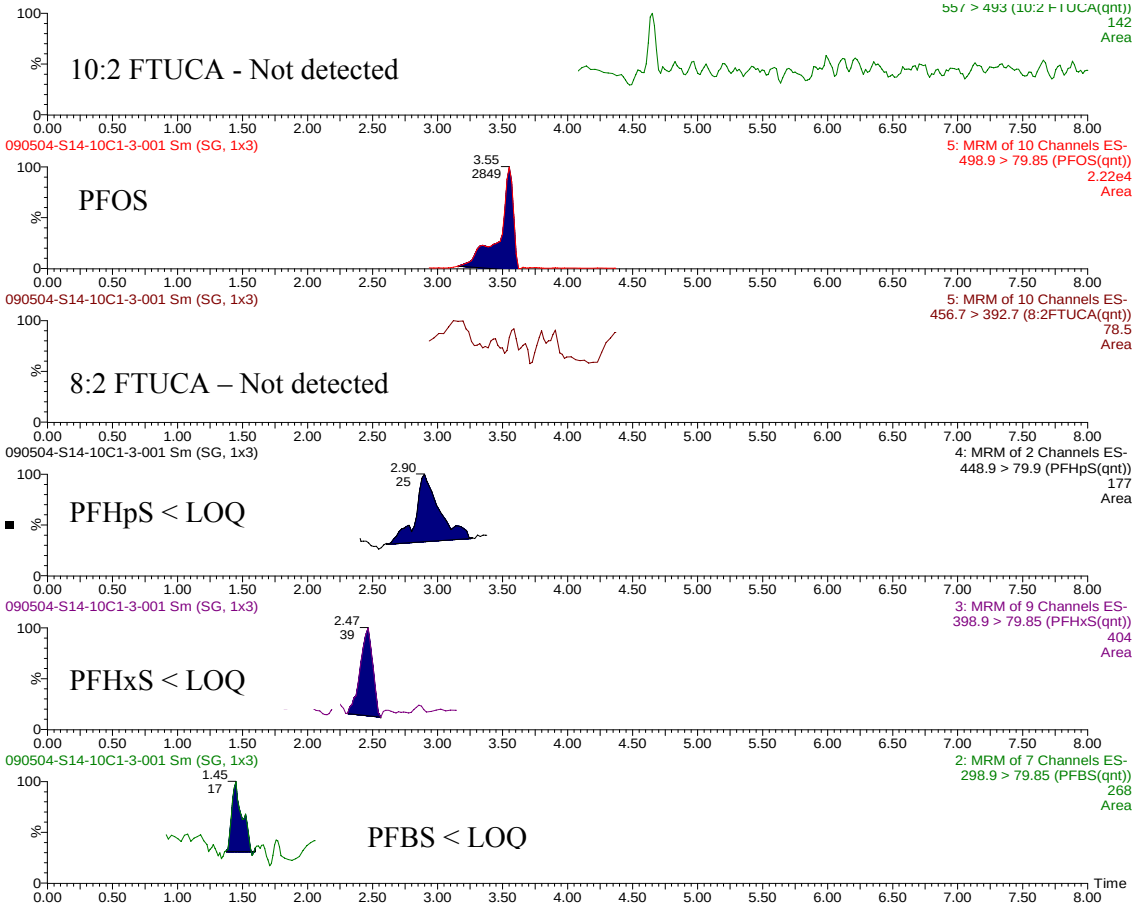
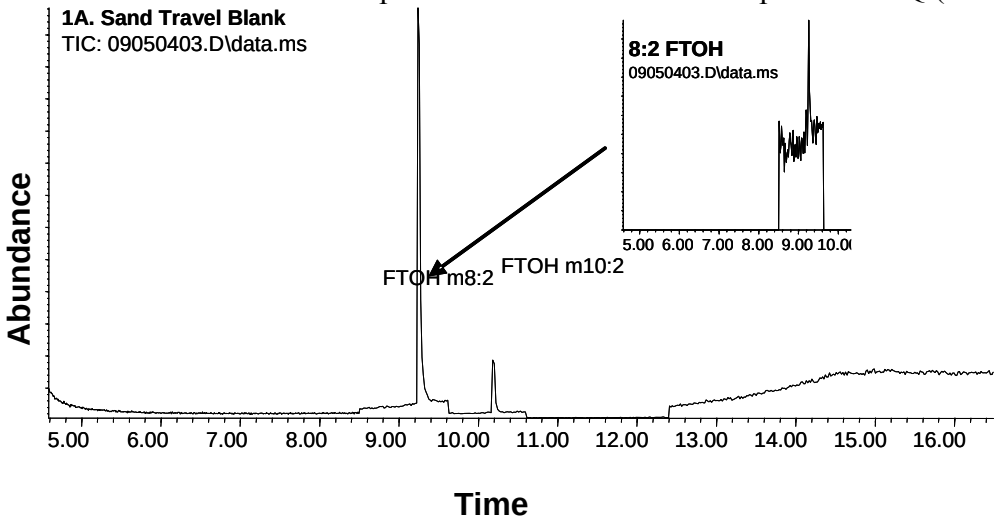


Figure 2. Chromatograms for FTOHs. Typical mass spectral data from trip blank samples (sand, 1A and Cowart soil, 1B), a FTOHs standard (1C), and a contaminated field sample (1D). Inlets are inserted for the clarity of chromatograms having close elution times. All FTOHs values from all trip blanks were less than its respective LOQ (refer Alcohols Table 1).



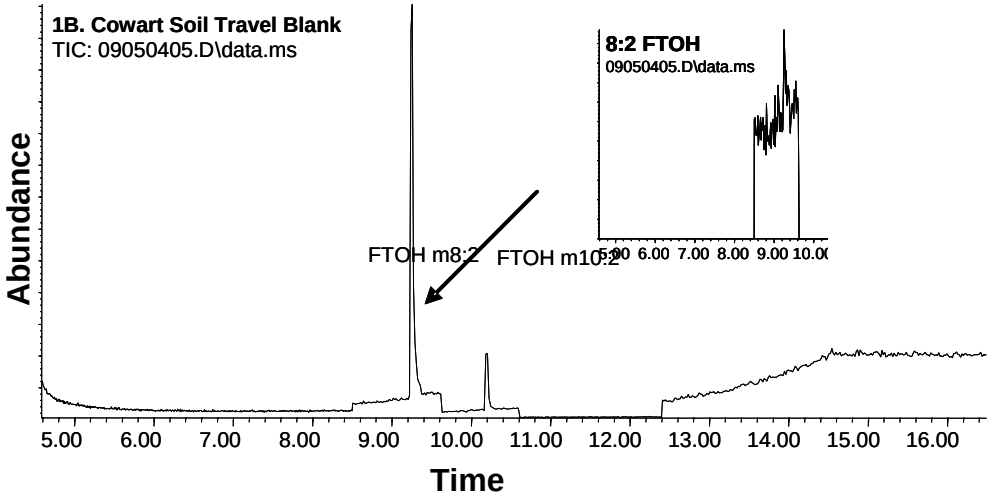
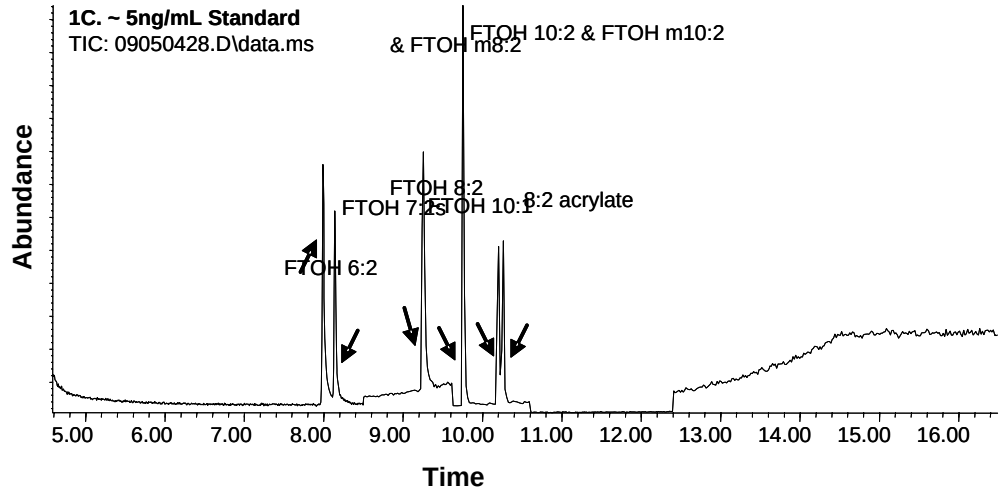


Figure 2. (continued)



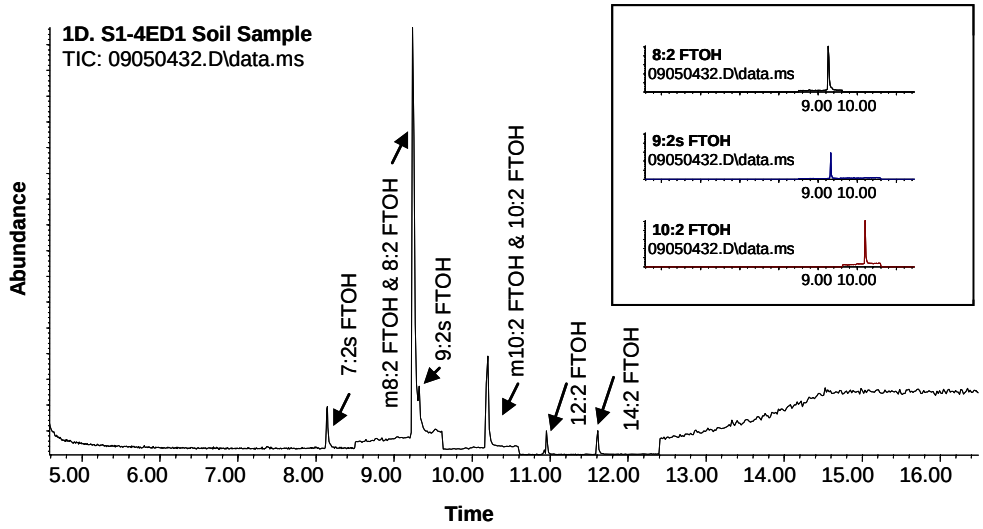


Figure 3. Identification of 14:2 FTOH in a Soil Extract. Two fragmented ions were monitored for quantitation $[M+1]^+$ (A) and qualification (loss of HF and H_2O) (B). Those fragmented ions are the major spectra for an anticipated elution period (C).

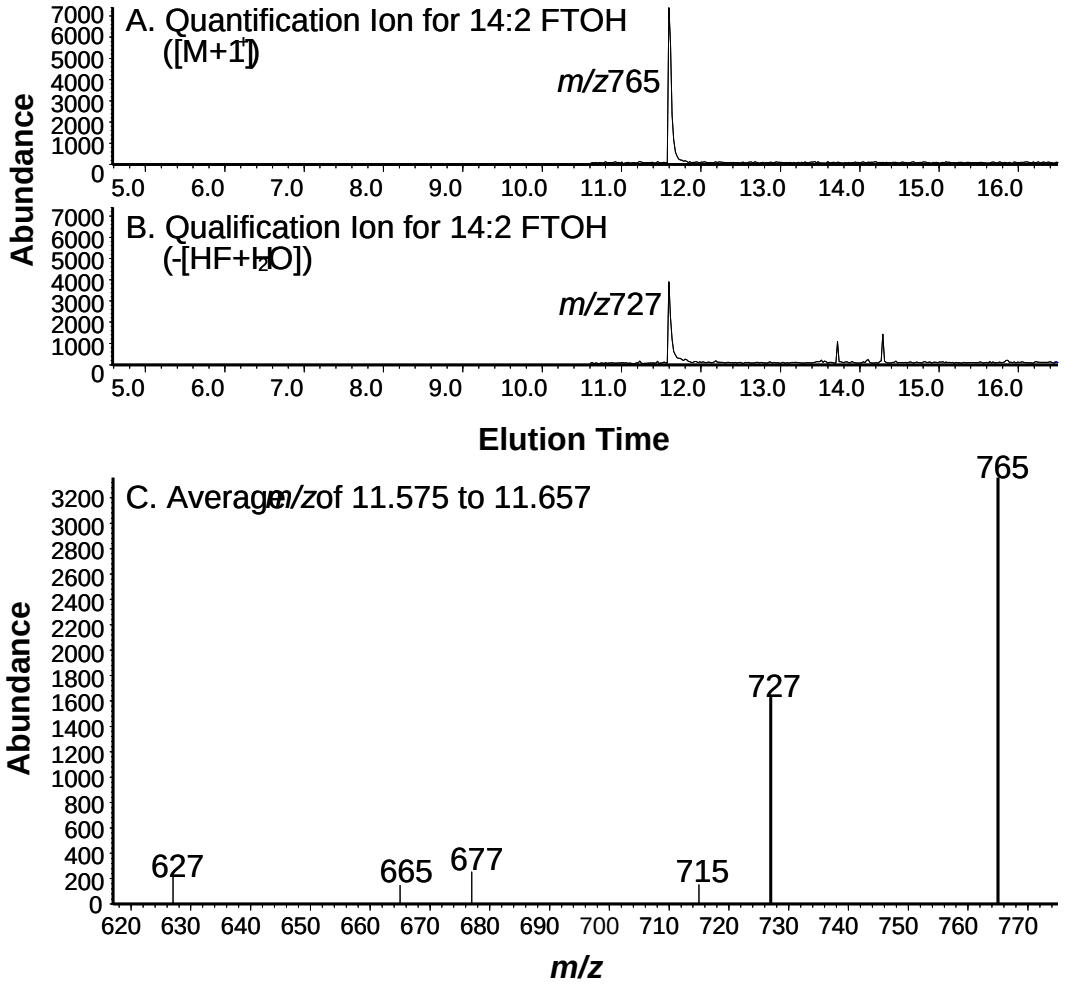
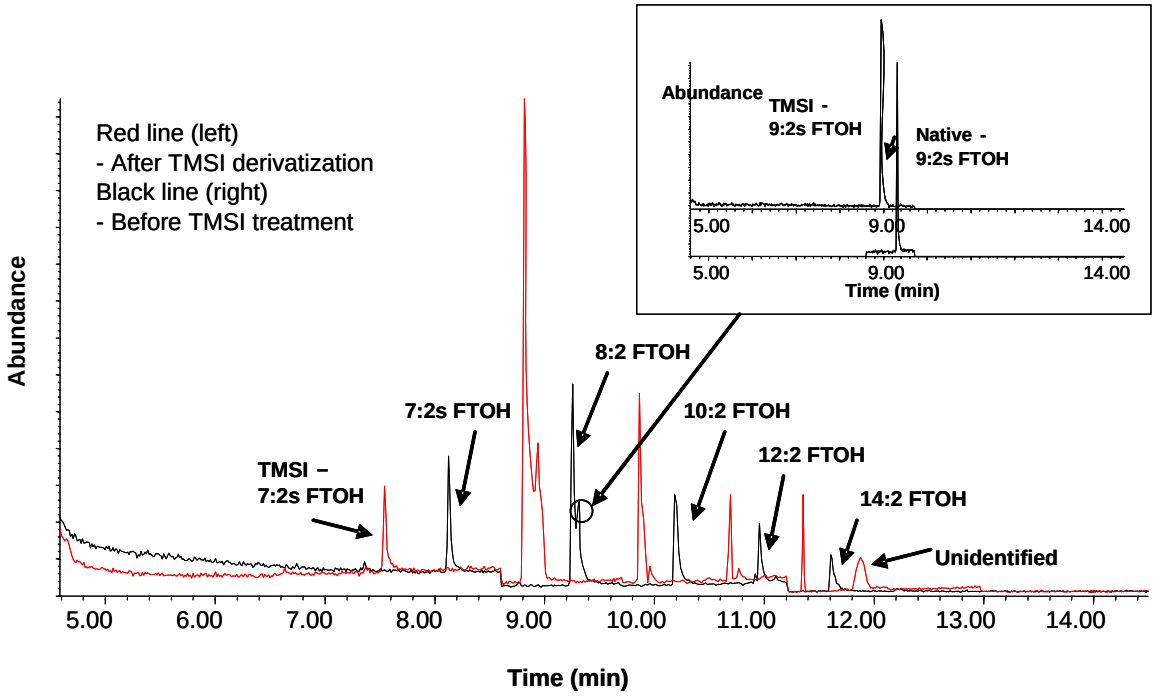


Figure 4. PCI-mode mass chromatograms of an extract of a Decatur soil before and after a TMSI derivatization. Only the largest peaks are identified for the purpose of clarity. Retention time of all target analytes shifted forward in time after the derivatization.



Appendices

Appendix 1: **SOP PMB 58.0:** Extraction of Fluorotelomer Alcohols from Sludge-Treated Soil Samples and Soils with High FTOH Concentrations

Appendix 2: **SOP PMB 59.0** Exhaustive Extraction of Perfluorinated Alkyl Acids (PFAAs) from Soil, Sludge-treated Soil and Sediment Samples with Ion-Pairing Cleanup

Appendix3: Liquid Chromatograph/Tandem Mass-Spectrometer Analysis Parameters

Appendix 4: Gas Chromatograph/Mass Spectrometer Analysis Parameters

(Note: While the cover sheets on the following pages are not signed, the hardcopies on file are signed.)

Appendix 1

U.S Environmental Protection Agency
Office of Research and Development

National Exposure Research Laboratory
National Center for Computational Toxicology
Research Triangle Park, North Carolina, Headquarters
Athens, Georgia
Cincinnati, Ohio
Las Vegas, Nevada

STANDARD OPERATING PROCEDURE

Title: **Extraction of Fluorotelomer Alcohols from Sludge-Treated Soil Samples and Soils with High FTOH Concentrations**

Number: PMB – 58.0	Effective Date: April 13, 2009

SOP was Developed X In-house ☐ Extramural

Alternative Identification:

SOP Steward

Name: John Washington

Signature: Date:

Approval

Name: J. MacArthur Long
Title: Chief, Processes and Modeling Branch

Signature: Date:

Concurrence*

Name:
Title:

Signature: Date:

SOP No.: PMB-58.0
Revision 0
Date: April 13, 2009
Page 1

Extraction of Fluorotelomer Alcohols from Sludge-Treated Soil Samples and Soils with High FTOH Concentrations

I. REAGENTS:

A. NPW (Nanopure Water)

1. Use laboratory de-ionized, 18MΩ (nanopure) water

B. Optima Grade MTBE

C. ($^{13}C_2$-$^{2}H_2$)8-2FTOH (m8-2FTOH) Extraction Recovery Stock Solution

Prepare from Wellington Certified Stock Solution in MTBE to give a concentration of 50 - 70 pg/µL m8-2FTOH.

D. ($^{13}C_2$-$^{2}H_2$)10-2FTOH (m10-2FTOH) Matrix Internal Standard Solution

Prepare two solutions in MTBE from Wellington Certified Stock Solution to give concentrations of 50 pg/µL and 5 pg/µL m10-2FTOH.

II. SOIL SAMPLE EXTRACTION

A. Determine Soil Sample Moisture Content.

1. Weigh three ~1-5 gram aliquots to tared weigh boats; vacuum dry over Drierite for 18 hours and weigh again.
2. Repeat step II.A.1 as needed until constant weight is obtained. Calculate percent moisture of soil.

B. Prepare & Extract Spiked Soil Sample

1. Charge 1g dry-weight equivalent of sludge-treated soil to pre-weighed (tube and cap) MeOH or MTBE -washed, 16-mL polypropylene copolymer (PPCO) centrifuge tubes with size-18 PPCO caps. Tubes were by rinsing/shaking capped tube 3X with 3mL MeOH, or by adding 5mL MTBE, capping and rotating overnight on Labquake Rotisserie Shaker.
2. Add sufficient NPW to achieve total H_2O content of 5 g, accounting for calculated moisture content of soil as added to the tubes. Weigh tube + soil + water
3. Add 3 mL of m8-2 FTOH spike solution, as recovery internal standard, to soil – water mixture, cap, and vortex. Weigh tube + soil + water + MTBE w/ spike.
4. Place tubes on Labquake Rotisserie Shaker and rotate for 15 to 24 hrs. Weigh again to compensate for any evaporation of MTBE.
5. Centrifuge in Sorvall at 37,000 x g and 18 to 22 ^{o}C for 30 min.
6. Freeze sample until water is frozen, transfer MTBE phase into tared 12 mL glass vial, and weigh vial plus extract.

C. Extract Spiked Soil Sample Three Additional Times with MTBE

1. Thaw centrifuge tube, reweigh, add 3 mL MTBE and reweigh again.
2. Repeat steps B.4 , B.5, and B.6, combining extract with that in 12 mL vial.
3. Repeat steps C.1 and C.2 twice more, for a total of 4 extractions.

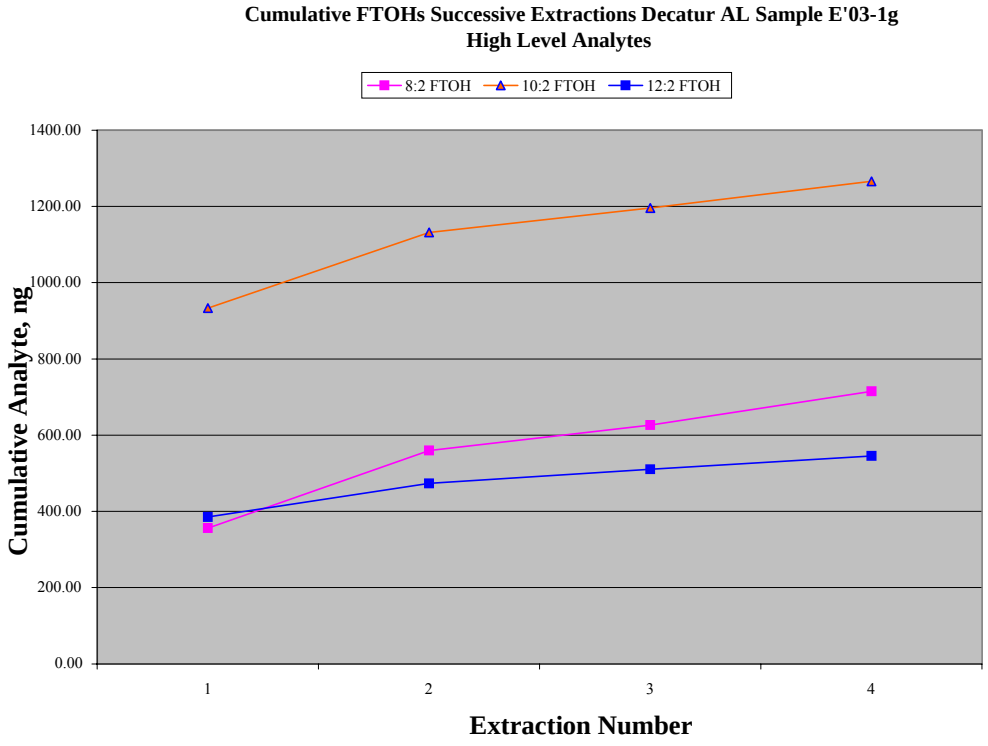
D. Prepare Combined Extract for GSMC Analysis

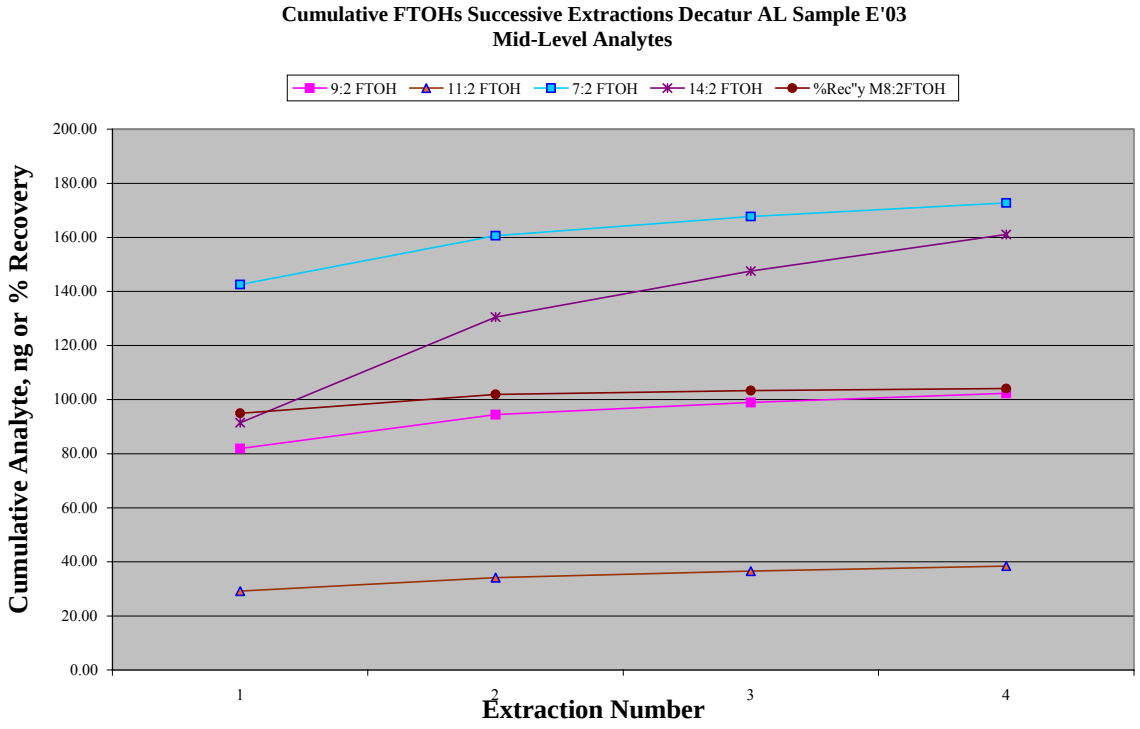
1. If no dilution is required, transfer 900uL combined extract from 12mL vial to tared (with cap) autosampler vial. Reweigh autosampler vial.
2. Add 100µL 50pg/µL m10:2 FTOH matrix internal standard stock solution to autosampler vial and reweigh again. Calculate concentration of m10:2 FTOH in pg/g and mass/mass dilution ratio.
3. If dilution is required, begin with 10X dilution. Transfer 100uL combined extract from 12mL vial to tared (with cap) autosampler vial. Reweigh autosampler vial.
4. Add 900µL 5pg/µL m10:2 FTOH matrix internal standard stock solution to autosampler vial and reweigh again. Calculate concentration of m10:2 FTOH in pg/g and mass/mass dilution ratio.
5. If additional dilution is required, repeat steps D.3 and D.4, using the previously diluted sample as a starting point.

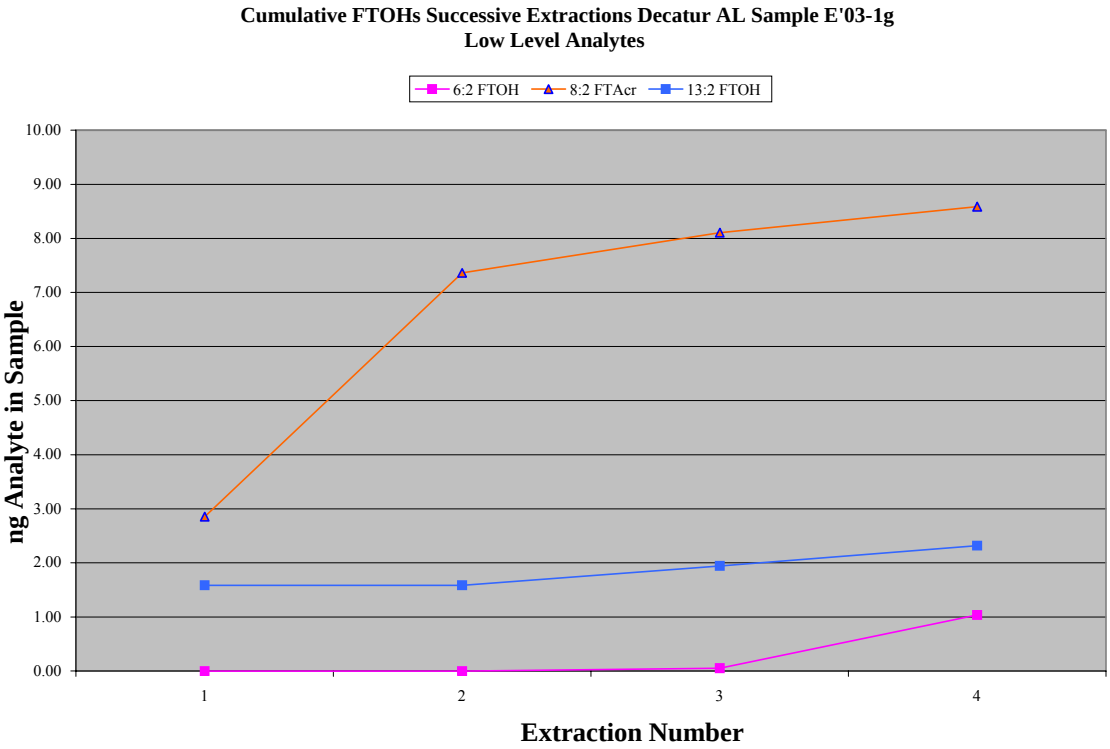
E. Extract storage

1. Store extract remainders in freezer using 36 section sample boxes, with appropriate labeling.

F. Example Multiple Extraction Results from SESD-07-0702-Sampling in Decatur, Alabama







Appendix 2

U.S Environmental Protection Agency
Office of Research and Development

National Exposure Research Laboratory
National Center for Computational Toxicology
Research Triangle Park, North Carolina, Headquarters
Athens, Georgia
Cincinnati, Ohio
Las Vegas, Nevada

STANDARD OPERATING PROCEDURE

Title: **Exhaustive Extraction of Perfluorinated Alkyl Acids (PFAAs) from Soil, Sludge-Treated Soil and Sediment Samples with Ion-Pairing Cleanup**

Number: PMB – 59.0	Effective Date: April 13, 2009

SOP was Developed X In-house ☐ Extramural

Alternative Identification:

SOP Steward

Name: John Washington

Signature: Date:

Approval

Name: J. MacArthur Long
Title: Chief, Processes and Modeling Branch

Signature: Date:

Concurrence*

Name:
Title:

Signature: Date:

SOP No.: PMB-59.0
Revision 0
Date: April 13, 2009
Page 1

Exhaustive Extraction of Perfluorinated Alkyl Acids (PFAAs) from Soil, Sludge-treated Soil and Sediment Samples with Ion-Pairing Cleanup

I. REAGENTS:

A. Polished Nanopure Water (PNPW)

2. To polish water, i.e., purge of PFCAs, use glassware system dedicated to water polishing.
3. Pass 2L 18MΩ (nanopure) water through a 60cc "Oasis HLB" cartridge (use the same cartridge no more than 3 times).
4. Store polished NPW in dedicated 1L containers.

B. Polished Tetrabutylammonium (TBA) Mix (Ion Pairing Reagent)

1. Prepare 0.50M Tetrabutylammonium Hydrogen Sulfate (TBAHS) in 18MΩ nanopure water.
2. Prepare 0.25M Na_2CO_3 in 18MΩ nanopure water.
3. Add 2.0 parts Na_2CO_3 solution to 1.0 part TBAHS solution, mixing slowly to avoid spillage due to CO_2 generation.
4. Place a 500mL Nalgene waste collection bottle in the reservoir of a Waters or comparable solid-phase extraction (SPE) vacuum system.
5. Mount a 60cc HLB cartridge on the port above the Nalgene bottle.
6. Flush with 50mL NPW and 50mL methanol, HPLC grade.
7. Replace the waste Nalgene bottle with a methanol-washed Nalgene bottle; and discard the waste.
8. Pass the TBA Mix in part I.B.3 through the cartridge until desired volume has been polished; cap and label polished TBA mix.
9. Flush cartridge with 50mL methanol (MeOH) per steps I.B.4 and I.B.6. Store in labeled Ziploc bag for further use in polishing this reagent mix only.

C. $^{13}C_8$-PFOA (M8C8) Extraction Recovery Spike Solution

1. Prepare from Cambridge Isotope Laboratories Certified Stock Solution in 60/40 (v/v) ACN/polished water to give a concentration of ~100 ng M8C8 per gram of solution.

D. $^{13}C_9$-PFNA (M9C9) Cleanup Recovery Spike Solution

1. Prepare from Wellington Certified Stock Solution in 60/40 (v/v) ACN/polished water to give a concentration of ~15 ng M9C9 per gram of solution.

E. $^{13}C_4$-PFOA (MC8) (and other mass-labeled perfluorinated compounds) mixed Internal Standard Solution (designated MMX)

1. Prepare from Cambridge Isotope Laboratories or Wellington Certified Stock Solutions in 60/40 (v/v) ACN/PNPW to give concentrations of ~100 pg/g for each mass-labeled internal standard per gram of solution. Internal standards chosen to match as many

individual PFAAs as possible, enabling individual isotopic dilution quantitation for each analyte.

F. 2.0 M NaOH Solution and 2.0M HCl Solution

1. Prepare from concentrated stock solutions using polished NPW.

II. SOIL SAMPLE EXTRACTION

A. Prepared 2mm Sieved Soil Sample

3. If necessary for handling, air dry bulk sample in hood in methanol-washed stainless-steel or glass container to a moisture content level which will enable the soil to be easily sieved – generally in the range of 20% water content.
4. Using all methanol-washed equipment, sieve using a 2mm stainless steel sieve, forcing soil as needed with large rubber stopper or nitrile-gloved hand. Store sieved soil in methanol-washed 500mL Nalgene bottle.
5. Weigh three ~1-5 gram aliquots to pre-weighed weigh boats; vacuum dry over Drierite for 18 hours and weigh again.
6. Repeat step II.A.3 as needed until constant weight is obtained. Calculate percent moisture of soil.
7. To prepare extraction sample:
    a. pass entire aliquot through 12-in diameter 2mm sieve;
    b. square and quarter in sieve pan using large spatula;
    c. remove three quarters and sieve to a second pan; return remainder to original container;
    d. square and quarter in sieve pan using large spatula;
    e. repeat steps c and d until size of aliquot is reduced to four grams;
    f. square and quarter final aliquot and charge to extraction tubes in part B.

B. Prepare Spiked Soil Samples

7. Charge 1g-dry weight equivalent of soil to pre-weighed (tube and cap) MeOH- or MTBE-washed, 16-mL polypropylene copolymer (PPCO) centrifuge tubes with size-18 PPCO caps. Re-weigh and record weight in data table.
8. Add 50uL 100 ng/g M8C8 spike solution to provide a loading of ~4 ng M8C8 per gram of dry soil. Reweigh.
9. Add 200uL 2.0M NaOH and allow to react for 30 min.
10. Add PNPW to achieve a total water content of 1.2g, compensating for soil moisture and water added in steps B.3 and C.2. Reweigh. Let stand for at least 30 min before proceeding to step C.1.

C. Extract Spiked Soil Samples

4. Add 1.8 mL ACN to yield a 60:40 by-volume solution of ACN:H_2O. Reweigh.
5. Add 200uL of 2.0M HCl to neutralize NaOH added in B.3. Reweigh.
6. Vortex until homogeneous appearance, sonicate for 60 min using ice to maintain lower bath temperature, transfer to Eberbach shaker table and shake on Low for 15 to 24 hrs, or rotate on Labquake rotisserie for 15-24 hours;

7. Centrifuge in Sorvall at 5,000 rpm and 18 to 22 ^{o}C for 20 min. Reweigh to capture solvent losses due to evaporation.
8. Decant liquid to 12mL pre-weighed (with top) glass vial. Reweigh both centrifuge tube and 12mL vial (with caps).
9. Add 3.0 mL 60:40 ACN/PNPW to centrifuge tube. Vortex, sonicate 60 min in ice, rotate or shake for 15-24 hours, centrifuge and reweigh.
10. Decant liquid to 12mL glass vial, combining with previous extracts, and reweigh vial.
11. Repeat steps C.5 and C.6 for a total of 4 extractions.
12. Evaporate contents of 12mL vial to dryness in SPE assembly, using nylon filters and 5-7 psi vacuum.

D. Cleanup Extract using Ion Pairing

1. Add 4 mL TBA Mix to dried extract from II.C.7. Vortex. Reweigh.
2. Add 5 mL methyl-tert-butyl-ether (MTBE). Vortex. Reweigh.
3. Freeze. Transfer MTBE to tared 12 mL glass vial. Reweigh.
4. Evaporate to dryness in SPE apparatus. Reweigh.
5. Reconstitute with 2mL 60/40 internal standard mix (MMX). Reweigh.

Appendix 3

Liquid Chromatograph/Tandem Mass-Spectrometer Analysis Parameters

Acetonitrile/water extracts of the soil aliquots were analyzed on a Waters Quattro Premier XE tandem mass spectrometer interfaced with a Waters Acquity ultra-performance liquid chromatograph (UPLC). Efforts have been made to reduce background noise in this system for PFOA by modifying the UPLC plumbing, including installing polyaryletheretherketone (PEEK) tubing, removal of the degasser, installation of a C18 trap column, 100 × 2.1 × 3.5 (mm length × mm inside diameter × um particle size) in the H_2O eluent line immediately upgradient of the solvent mixer, and using manually-degassed 18 MΩ H_2O that has been 'polished' by passing through a Waters HLB™ solid phase extraction cartridge (Washington et al., 2008b).

When preparing for sample analysis, it was discovered that the liquid chromatograph could not maintain a sufficiently stable eluent pressure, with pressure variation of >1000 pounds per square inch (PSI), much in excess of the desired range of a few 10s of PSI. After cleaning and replacing many pressure-control components, it was determined that the only way to achieve satisfactory pressure stability, within an acceptable sample-analysis timeframe, was to remove the trap column. With the trap column removed, the operating pressure range dropped about 2000 PSI and stabilized the pressure variability, as desired, but it also altered the elution time windows for the analytes.

All system operations were controlled by Waters MassLynx 4.1 and QuanLynx 4.1. Twenty microliters of extract were introduced into a 50-uL loop using 'partial loop with needle overfill' mode to a Waters BEH C18 guard cartridge followed by a Waters BEH C18 analytical column, 100 × 2.1 × 2.1, maintained at 35 ^{o}C. The UPLC was operated using ACN and water eluents adjusted to pH 4 with glacial acetic acid. Pumping at a constant total flow of 0.5 mL/min, runs were started with 35% ACN, and then linearly ramped to 90% ACN over 5 min, held for 6 min, linearly ramped back to 35% ACN at 11.1 min, from which time the composition was held constant until the end of analysis at 13 min.

After UPLC elution, extracts were introduced to the mass spectrometer operated in ESI(-) mode with the capillary potential set at -600 V, the extractor potential at -2 V and the radio-frequency (RF) lens potential at 0.3 V. The source temperature was maintained at 140 ^{o}C. The N_2 generator desolvation gas was maintained at 350 ^{o}C and 800 L/h flow. The cone gas flow, also supplied by the N_2 generator, was set to 25 L/h. Analyte-specific instrumental parameters, including monitored transitions, were optimized for PFCs analysis. The low- and high-mass resolutions in the first quadrupole both were set to 13.0 (unitless ratio of direct to RF current voltages) and the ion energy was set to 0.7 eV. In the collision cell, the entrance was set to -3 V, the interior set to -16 V and the exit set to -1 V. The Argon collision gas was set to flow at 0.45 mL/m. Low- and high-mass resolutions in the third quadrupole both were set to 12.0 and the ion energy was set to 1.0 eV. The detector was operated in multiple-reaction-monitoring (MRM) mode, with the detector multiplier set to -700 V and the dwell time was set to 70 ms with the objective of achieving at least 15 scans per peak.

Chromatograms were smoothed using a second-order Savitsky-Golay algorithm and two five-point smoothes with a few exceptions to accommodate monitoring the high number of transitions in the method. Unless otherwise noted, quantitation was performed using mass-labeled matrix internal standards. Having mass-labeled standards for C6, C8 ($^{13}C_4$-PFOA), C9, C10, C11, and C12, the analytes were quantitated using isotopic dilution. C7 and PFOS were quantitated using the mass-labeled C8 ($^{13}C_4$-PFOA) and $^{13}C_2$-PFDA matrix internal standard, respectively. Calibrations were constructed with linear regressions of untransformed data, and plots of peak area/internal standard area versus calibration standard concentration/ internal standard area; 1/X weighting was applied for regression. Calibration curves consisted of 12 to 14 concentrations of the targeted species spanning 0.9 to 4800 pg/g. Standards were randomly interspersed with sample extracts and blanks throughout the sample runs. The limit of quantification (LOQ) was designated as the value of the lowest standard for which all standard readings included in the calibration are within specified tolerances **(Table 2)** of the prepared standard value. **Table 3** summarizes the extract dilution factors. The efficacy of the acids extractions was monitored using $^{13}C_8$-PFOA as a recovery internal standard

Appendix 4

Gas Chromatograph/Mass Spectrometer Analysis Parameters

Methyl *tert*-butyl ether (MTBE) extracts of the soil aliquots were analyzed on an Agilent Technologies (Palo Alto, CA) 6890N GC system equipped with a 5973N mass selective detector (MSD). The MSD was operated in the positive chemical-ionization (PCI) mode with methane reagent gas for quantitative analyses. All system operations were controlled by Enhanced Chemstation D.02.00275. Compound separation and quantification were performed on a Restek (Bellefonte, PA, USA) Rtx-1701 capillary column, 30m × 0.25mm I.D. × 0.25μm film thickness with a 10m deactivated Integra-Guard™ guard column as the inlet. Sample volumes of 1 μL were injected in the pulse-splitless mode at 40 PSI for 0.90 s into a 4mm ID gooseneck inlet liner. GC system inlet and MS interface temperatures were set at 140 ^{o}C and 290 ^{o}C, respectively. The column temperature was programmed as follows: held at 60 °C for 1 min, and then ramped up at 3 °C/min to 75 °C, then at 20 °C/min to 185 °C with ballistic heating to a final temperature of 260 °C, which was held for 6 min. The helium carrier gas was at a constant flow of 1 ml/min. The MSD operating parameters were routinely set by the tune file. EM potential was set at + 2200 volts. MS source temperature was set at 250 ^{o}C and the quadrupoles at 150 ^{o}C. A selected-ion monitoring (SIM) program was constructed, in which quantifying ions $[M + 1]^+$ and qualifying fragment ions were specified, was constructed with the analytes being separated into groups based on elution times of the FTOHs.

A total of eleven GC/MS analytes were investigated for their presence in the sludge-applied soils. Calibration curves were constructed using a mass-labeled matrix internal standard for all analytes, $^{2}H_{2}{}^{13}C_{2}$-10:2 FTOH (M10:2 FTOH). Commercial standards do not exist for some analytes, therefore these were quantified using standard curves for similar compounds in the homologous series. The analyte (and standard curve it was quantified on) are 9:2s-FTOH (8:2 FTOH), 11:2s-FTOH (10:2 FTOH), 12:2 FTOH (10:2 FTOH), 13:2s-FTOH (10:2 FTOH) and 14:2 FTOH (10:2 FTOH). In the absence of authentic standards, the identity of these compounds, tentatively identified by loss of *m/*z 38 ($HF + H_2O$) from the $[M + 1]^+$ ion, was confirmed using trimethylsilylimidazole (TMSI) derivatization (Ellington et al., 2009). The limit of quantitation (LOQ) was determined using a signal/noise ratio (S/N>3) and the lowest acceptable standard concentration within ±30% of its theoretical value. The efficacy of the alcohols extractions was monitored using $^{2}H_{2}{}^{13}C_{2}$-8:2FTOH (M8:2 FTOH) as a recovery internal standard